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A PRECISION APPARATUS FOR APPLYING LIQUIDS TO TEST SURFACES[1]

BY E. E. BUCKHOLZ

ABSTRACT

A precision apparatus for applying liquids to test surfaces has been described. It will deliver up to five milliliters of liquid in droplets of uniform size. The mean diameter of the droplets can be varied from 0.3 to 1.6 mm.

INTRODUCTION

In the course of work at Suffield Experimental Station it became desirable to apply known volumes of liquid in discrete droplets to fabrics, filter paper, and other test surfaces. Since the required equipment could not be obtained commercially it was decided to build an apparatus in our laboratory. The present report describes this apparatus. It has proved to be very effective for our purposes and might be of value to research workers in other fields. It is particularly suitable for handling noxious chemicals, since besides being capable of delivering known volumes of liquid in uniform droplets it is sufficiently small to fit into a fume cupboard where it can be operated by remote control.

DESCRIPTION

The apparatus employs a 5-ml. syringe fitted with a No. 27 gauge hypodermic needle, and around the latter is fixed an air nozzle. The plunger of the syringe is depressed automatically at a fixed rate and the size of the droplets is controlled by varying the air flow through the nozzle. The syringe with needle and air nozzle is mounted on a carriage which is moved back and forth along a right- and left-hand threaded cam. When the carriage reaches either end of this cam, it is shifted forward a small distance. Thus a rectangular pattern of droplets is delivered onto the test surface beneath, the drops being spaced evenly in lines. Working drawings of the apparatus are given in Figs. 1, 2, and 3, and a photograph is shown in Fig. 6.*

[1]*Manuscript received July 19, 1956.*

Contribution from the Physiology Section, Suffield Experimental Station, Defence Research Board, Ralston, Alberta. Issued as Suffield Technical Paper No. 82, Project No. D52-89-50-15.

**The electric timer shown at the extreme right of the photograph, Fig. 6, is not described as a part of the apparatus.*

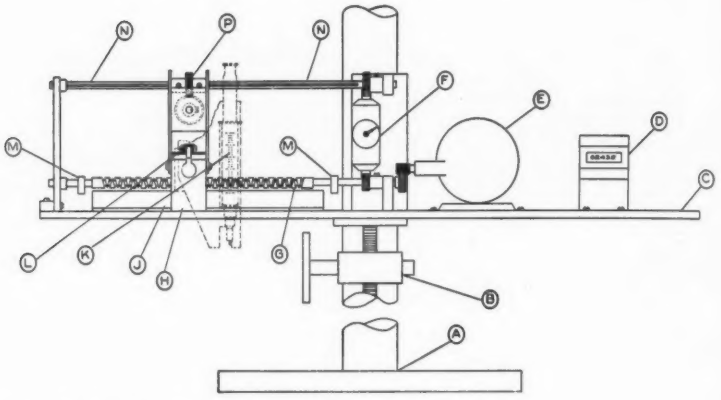


FIG. 1. Spray assembly support and drive.

A. Metal stand
B. Rack and pinion
C. Platform
D. Electrical counter
E. Motor (1/100 hp.)
F. Variable speed transmission
G. Right- and left-hand threaded cam
H. Carriage block
J. Guide bar
K. Spray assembly (in broken lines)
L. Forward shift device
M. Eccentric disks
N. Cross drive shaft
P. Helical gear

A front view of the apparatus is shown in Fig. 1. A heavy metal stand (A), is fitted with a rack and pinion (B), which permits the raising or lowering of a platform (C). The platform supports an electrical counter (D), a 1/100 hp. ratio motor (E), and a variable speed transmission (F)* with a readily adaptable 6 to 1 and 1 to 6 ratio. The motor drives a right- and left-hand threaded cam (G), machined on a steel shaft, 7.875 in. in length, with four threads to the inch, which in turn drives the carriage block (H) back and forth along a guide bar (J). The block supports the spray assembly (K) (sketched in broken lines) and the forward shift device (L). The latter is automatically tripped by two eccentric disks (M), which are fixed one at each end of the threaded cam (G).

The variable speed transmission (F), driven by the threaded cam shaft (G), actuates the cross drive shaft (N). This shaft has a 1/16 in. groove machined along its entire length. As the shaft (N) rotates, it drives a right-angle helical gear (P), and at the same time allows the gear, maintained by the carriage block (H), to slide from end to end along the shaft (N).

Fig. 2 shows the syringe and spray attachment, both from the front and side. The principal parts are: the carriage block (A) (shown in Fig. 1 as H), the guide bar way (B), and the right- and left-hand threaded cam way (C). The setscrews (D) at the right and left side of the block (A) (showing right side only in Fig. 2) are set so that when in contact with the eccentric disks at either end of the threaded cam, they will engage the tongue (E) in the rack on the spray assembly shaft (F) and shift the assembly forward a preset distance. At the end of the spray assembly shaft (F), there is mounted a plastic plate (G),

**Manufactured by the Metron Instrument Co., Denver, Colorado.*

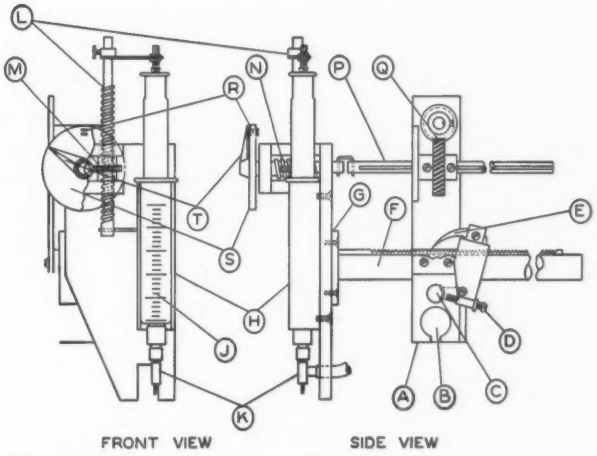


FIG. 2. Spray assembly.

A. Carriage block
B. Guide bar way
C. Right- and left-hand threaded cam way
D. Setscrews
E. Tongue
F. Spray assembly shaft
G. Plate
H. Trough
J. Syringe
K. Air nozzle
L. Threaded shaft
M. Combination gear
N. Worm gear
P. Drive shaft
Q. Helical gear
R. Electrical contacts
S. Dial
T. Dial hand

to which is secured a trough (H) supporting the syringe (J) with the accompanying No. 27 hypodermic needle and air nozzle (K).

The plunger of the syringe is depressed by an arm leading from a threaded shaft (L), which is driven by an internal–external combination gear (M). This gear is actuated by a worm gear (N) of 30 to 1 ratio connected in line to the drive shaft (P). This shaft also has a 1/16 in. groove machined full length to allow it to move with the spray attachment when the forward shift takes place; at the same time it is actuated by means of the right angle helical gear (Q), which is driven by a right angle gear of 3 to 2 ratio shown as (P) in Fig. 1. Electrical contacts (R) are mounted on a plastic dial (S), shown in both front and side view, Fig. 2. The dial hand (T) is fitted on the end of the worm gear shaft (N). The hand brushing over the electrical contacts (R), at each rotation, registers the revolutions on the counter (D) (Fig. 1) through electrical impulses from 115 v. line.

A cross section of the spray nozzle (K) is shown in Fig. 3. The length of the

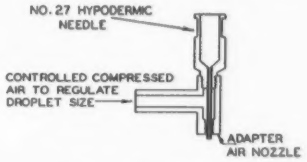


FIG. 3. Spray nozzle.

nozzle is 14 mm. and its diameter is 4.5 mm., and the size of the annular ring through which the air issues is 0.8 mm.

CALIBRATION OF VOLUME DELIVERED

The apparatus was calibrated by determining the weight of distilled water which was delivered at a fixed setting of the variable speed transmission for a given number of revolutions, viz. 111, of the counter. The droplets were caught and weighed. Twelve determinations were made: the extreme values were 0.9932 and 0.9705 gm., the mean was 0.9825 gm., and the standard deviation was 0.0007 gm.

MEASUREMENT OF DROPLET SIZE

The size of the droplet which falls from the syringe needle depends on the rate of flow of air from the nozzle (K), Fig. 2. The flow of air from a compressor is controlled by a regulating needle valve, and the rate of flow is measured with a flowrator. Depending on the rate of air flow, drops ranging in size from 0.32 mm. to 1.6 mm. in diameter can be obtained. With the present apparatus drops smaller than 0.32 mm. in diameter tend to break up. A photograph of stain sizes obtained at different rates of air flow is shown in Fig. 4.

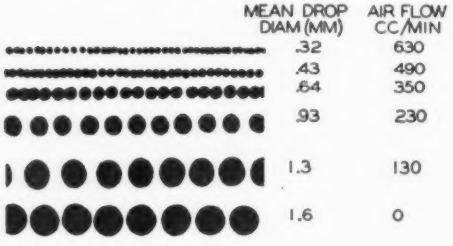


FIG. 4

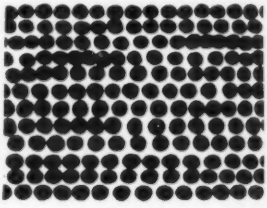


FIG. 5

FIG. 4. Different stain sizes of droplets delivered by apparatus. Diameter of droplet and setting of flowrator, on right.

FIG. 5. Section of typical spray pattern, droplet 1.0 mm. in diameter.

An indication of the uniformity of the size of the droplet for each of six different rates of air flow was obtained by determining the average diameter of a number of stains and calculating the standard and per cent deviations. For each stain, two diameters, at right angles to one another, were measured to the nearest 0.01 mm. and the average recorded. The results of this study are given in Table I. The standard deviations, expressed as a percentage of the

TABLE I

MEAN STAIN SIZES WITH STANDARD DEVIATIONS FOR DIFFERENT RATES OF AIR FLOW

Air flow (cc./min.)	Number of stains measured	Mean diameter (mm.)	Standard deviation	Per cent deviation
630	15	1.86	.08	4.3
490	11	2.54	.04	1.5
350	16	3.85	.05	1.3
230	9	5.59	.13	2.3
130	7	8.40	.10	1.2
0	7	9.69	.05	0.5

mean stain diameter, varied from only 0.5 to 4.3 for the six different drop sizes. Because of the known variations in spreading, the uniformity of the droplets as delivered by the apparatus must be of a high order.

OPERATING PROCEDURE

The syringe is filled with liquid and placed in the plastic trough, and the plunger drive adjusted so that it makes contact with the head of the plunger. The air is turned on, and the flow adjusted to give the required droplet size. Experiments to date have been made primarily with droplets approximately 1 mm. in size. The test surface, fastened to a small table, is placed inside the fume cupboard beneath the spray assembly attachment, which is moved to the extreme right-hand end of the threaded cam (G) (Fig. 1), and the test surface adjusted so that the first droplet will fall at its upper right-hand corner. When everything is in position, the door of the fume cupboard is partially closed.

The motor driving the spray assembly mechanism is now switched on from outside the fume cupboard, and droplets begin to fall in a straight line as the spray assembly attachment moves along the threaded cam. When the spray assembly reaches the left-hand end of the cam, it is moved forward a distance of 0.3 to 0.9 cm. by the shift and tripping device (L) (Fig. 1) and starts its return movement, leaving a second line of droplets parallel to the first.

A rectangle of droplets is thus formed (see Fig. 5), the maximum length of which is fixed by the threaded cam (G) (20 cm.) and the width by the assembly shaft (F) (max. 9 cm.). In practice an area of 140 cm.^{2} (20×7) was used. As the set screws (D) of the shift and tripping device (L) were adjusted to give a

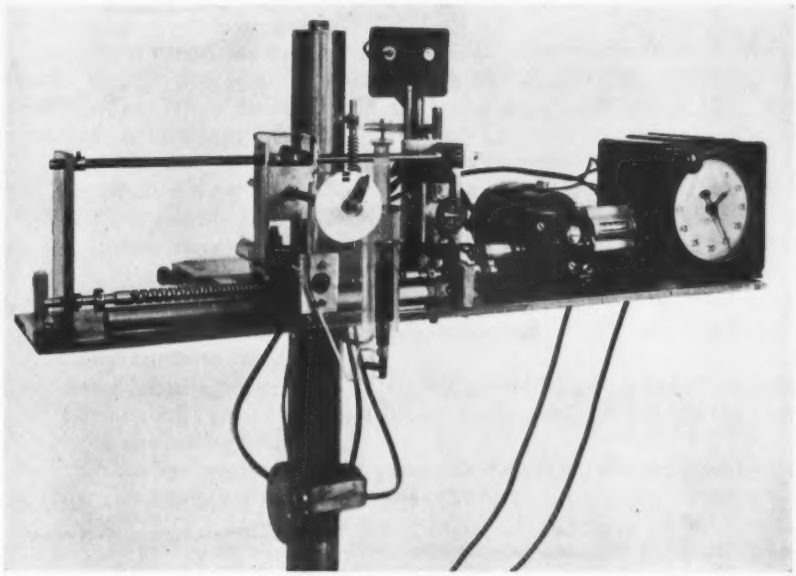


FIG. 6. Spray apparatus.

forward shift of the spray assembly of 0.64 cm., 12 rows of droplets were put down on the area. The assembly moved horizontally at 1.7 cm. per sec. and therefore the spray time was two minutes, 21 seconds.

The rate at which the droplets are delivered is controlled by the variable speed transmission and the volume is measured by the revolutions of the counting dial. One milliliter is delivered for every 111 revolutions of the counter. As it was customary to use the same spray area for all volumes (0.2 to 5.0 ml.) of liquid delivered, the plunger was set to deliver the required volume in exactly two minutes, 21 seconds. When this was done it was found that for the smallest volume the droplets fell 1.7 cm. apart, and fell proportionally closer together as the volume was increased.

ACKNOWLEDGMENT

I wish to express my thanks to Dr. M. K. McPhail for his interest in this work and for his help with the preparation of the manuscript.

ESTIMATION OF IDEAL GAS HEAT CAPACITIES OF HYDROCARBONS[1]

By A. I. Johnson and Chen-Jung Huang

ABSTRACT

From the data of the American Petroleum Research Institute Project 44 equations relating group contributions of heat capacity for the ideal gas state to temperature were obtained. These contributions are easily summed to yield equations relating ideal gas heat capacity of hydrocarbons to temperature over the range 300° K. to 1500° K. The accuracy of the equations is good and their use for interpolation is easy.

INTRODUCTION

In reactor design and other process calculations chemical engineers often require analytical relationships between heat capacity and temperature. Such an equation is provided by the calculation of bond contributions, the Einstein functions of which are expressed as quadratic equations. Unfortunately the equations obtained by the Dobratz method (2) do not hold above about 700° K.

Later Stull and Mayfield (4) proposed modified bond contributions which hold up to 1500° K. and also take into account some different types of double bond. This method permits fairly easy estimation of ideal gas heat capacities at 50° intervals between 250° K. and 500° K. and at 100° intervals thereafter to 1500° K. Their procedure does not provide an analytical relationship between temperature and heat capacity.

PROCEDURE

Group heat capacities were obtained at four temperatures from the A.P.I. tables (1). The temperatures selected were 300° K., 400° K., 1000° K., and 1500° K. The values obtained and the compounds from which they were estimated are indicated in Table I.

The A.P.I. tables indicate that uniform increments for each CH_2— group exist for the normal paraffins, alkyl cyclohexanes, acetylenes, and other series. The —CH_2— contribution of Table I is based on the normal paraffin series starting from ethane, although the tables indicate that a slight discrepancy may exist for the lower members of the series.

Contributions of the CH_2= group were obtained from ethylene only. The values so obtained resulted in uniform contributions for the group —CH= for the series propene to decene.

Similarly contributions of the CH≡ group were based on acetylene only. Use of these values gave almost equal contributions of —C≡ from the series propyne to nonyne.

In a similar manner, using the compounds indicated, the contributions of the other groups shown in Table I were obtained.

[1]*Manuscript received August 23, 1956.*
Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ontario.

TABLE I

OBSERVED AVERAGE INCREMENTS

Group	300° K.	400° K.	1000° K.	1500° K.	Based on
$-CH_2-$	5.48	6.94	12.35	14.28	Ethane to eicosane
CH_3-	6.23	7.85	14.73	17.48	Ethane to decane
$CH_2=$	5.23	6.45	11.29	13.18	Ethylene
$-CH=$	3.87	4.89	8.43	9.72	Propene to decene
	19.41	25.98	47.66	54.38	Toluene to octyl-benzene
$CH\equiv$	5.27	5.99	7.96	8.85	Acetylene
$-C\equiv$	2.86	4.23	4.83	5.39	Propyne to nonyne
	4.68	6.16	10.18	11.53	2-Methyl-propane 2-Methyl-butane 2-Methyl-pentane 2-Methyl-hexane 3-Methyl-pentane
$-CH_2-$ 6-membered ring	4.26	5.97	12.63	14.77	Cyclohexane
$-CH_2-$ 5-membered ring	4.00	5.65	11.95	14.18	Cyclopentane
	3.64	5.34	8.48	8.33	1,1-Dimethyl-cyclopentane 2,2,3-Trimethyl-butane 2,2-Dimethyl-butane
	3.13	3.86	5.91	6.37	2-Methyl-propene 2-Methyl-2-butene 1,2-Dimethyl-cyclopenten

Using the four values for each group shown in Table I a cubic equation representing the contribution as a function of the absolute temperature in degrees Kelvin was calculated. These are listed in Table II.

TABLE II

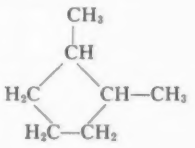
EQUATIONS RELATING GROUP CONTRIBUTIONS AND TEMPERATURE

Group					
$-CH_2-$	$C_p^\circ =$	-0.186	$+ 2.243\times10^{-2}T$	$-0.1263\times10^{-4}T^2$	$+0.00274\times10^{-6}T^3$
CH_3-	$C_p^\circ =$	0.427	$+ 2.183\times10^{-2}T$	$-0.0863\times10^{-4}T^2$	$+0.00111\times10^{-6}T^3$
$CH_2=$	$C_p^\circ =$	0.662	$+ 1.770\times10^{-2}T$	$-0.0874\times10^{-4}T^2$	$+0.00167\times10^{-6}T^3$
$-CH=$	$C_p^\circ =$	-0.239	$+ 1.663\times10^{-2}T$	$-0.1056\times10^{-4}T^2$	$+0.00260\times10^{-6}T^3$
	$C_p^\circ =$	-7.576	$+11.007\times10^{-2}T$	$-0.729\times10^{-4}T^2$	$+0.01801\times10^{-6}T^3$
$CH\equiv$	C_p°	2.017	$+ 1.400\times10^{-2}T$	$-0.1157\times10^{-4}T^2$	$+0.00352\times10^{-6}T^3$
$-C\equiv$	$C_p^\circ -$	-5.252	$+ 3.887\times10^{-2}T$	$-0.4400\times10^{-4}T^2$	$+0.01521\times10^{-6}T^3$
$-CH$	$C_p^\circ =$	-1.942	$+ 2.832\times10^{-2}T$	$-0.2281\times10^{-4}T^2$	$+0.00661\times10^{-6}T^3$
$-CH_2-$ (6-ring)	$C_p^\circ =$	-2.137	$+ 2.473\times10^{-2}T$	$-0.1195\times10^{-4}T^2$	$+0.00198\times10^{-6}T^3$
$-CH_2-$ (5-ring)	$C_p^\circ =$	-2.318	$+ 2.471\times10^{-2}T$	$-0.1294\times10^{-4}T^2$	$+0.00257\times10^{-6}T^3$
	$C_p^\circ =$	-4.655	$+ 3.682\times10^{-2}T$	$-0.3551\times10^{-4}T^2$	$+0.00982\times10^{-6}T^3$
	$C_p^\circ =$	-0.0535	$+ 1.342\times10^{-2}T$	$-0.1019\times10^{-4}T^2$	$+0.00273\times10^{-6}T^3$

EXAMPLES OF THE USE OF THE EQUATIONS

Two examples of the use of the equations follow. These calculations can be carried out very easily using a desk calculator.

1,2-Dimethyl-cyclopentane



$$2\ CH_3 \quad 2(C_p^\circ = 0.427 + 2.183\times10^{-2}T - 0.0863\times10^{-4}T^2 + 0.00111\times10^{-6}T^3)$$

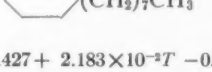
$$2\text{—}CH \quad 2(C_p^\circ = -1.942 + 2.832\times10^{-2}T - 0.2281\times10^{-4}T^2 + 0.00661\times10^{-6}T^2)$$

$$3\text{—}CH_2\text{—} \quad 3(C_p^\circ = -2.318 + 2.471\times10^{-2}T - 0.1294\times10^{-4}T^2 + 0.00257\times10^{-6}T^3)$$

$$\text{Summing:} \quad C_p^\circ = -9.984 + 17.443\times10^{-2}T - 1.017\times10^{-4}T^2 + 0.02315\times10^{-6}T^3$$

Comparison of calculated and tabulated values:

Temperature, °K.	C_p°	
	Calculated	Tabulated
300	33.82	32.34
1000	85.89	85.57
1300	95.76	95.39

n-Octyl-benzene 

$$CH_3\text{—} \quad (C_p^\circ = 0.427 + 2.183\times10^{-2}T - 0.0863\times10^{-4}T^2 + 0.00111\times10^{-6}T^3)$$

$$7\text{—}CH_2\text{—}7 \quad (C_p^\circ = -0.186 + 2.243\times10^{-2}T - 0.1263\times10^{-4}T^2 + 0.00274\times10^{-6}T^3)$$

$$\text{—} \quad (C_p^\circ = -7.536 + 11.007\times10^{-2}T - 0.7290\times10^{-4}T^2 + 0.01810\times10^{-6}T^3)$$

$$\text{Summing:} \quad C_p^\circ = -8.411 + 28.891\times10^{-2}T - 1.6994\times10^{-4}T^2 + 0.0385\times10^{-6}T^3$$

Comparison of calculated and tabulated values:

Temperature, °K.	C_p°	
	Calculated	Tabulated
300	64.00	64.07
1000	148.85	148.8
1300	164.11	164.5

Table III compares calculated results for 17 compounds with A.P.I. data (1). All values are for 1300° K., to illustrate the use of the equations for interpolation. Except for 3,3-dimethyl-1-butene and cyclohexene the agreement is good.

TABLE III

COMPARISON OF CALCULATED $C_p°$ VALUES WITH A.P.I. DATA AT 1300° K.

Compound	Calculated value	A.P.I. value	% Deviation
Methyl-acetylene	29.39	30.50	3.6
1-Butene	52.12	52.16	0.1
n-Octane	115.20	115.2	0.0
Toluene	68.68	68.77	0.1
Methyl-cyclohexane	98.29	98.8	0.5
1,2-Dimethyl-cyclopentane	95.76	95.39	0.4
3,3-Dimethyl-1-butene	71.43	79.51	10.2
Cyclohexene	81.28	73.92	9.9
3-Methyl-1-butene	65.98	66.28	0.5
2-Methyl-1-butene	65.72	66.02	0.5
2-Methyl-2-butene	65.39	65.42	0.0
1,3-Dimethyl-cyclopentene	86.74	85.6	1.3
n-Butyl-cyclopentane	122.78	122.8	0.0
3,3-Dimethyl-cyclopentene	87.13	86.9	0.3
n-Octyl-benzene	164.11	164.5	0.2
Ethyl-benzene	82.23	82.57	0.4
2,2,3-Trimethyl-butane	102.30	102.4	0.1
		Average	1.7

Tables I and II do not include a contribution for H— so that the method does not hold for some common hydrocarbons such as methane or benzene. It may be noted that the method of Stull and Mayfield also does not hold for the first members of some series and like the contributions proposed in this paper does not include differences between some isomers.

Table IV compares several values obtained using the proposed contributions with those obtained by Stull and Mayfield.

TABLE IV

COMPARISON OF CALCULATED $C_p°$ VALUES WITH A.P.I. DATA AND WITH STULL AND MAYFIELD

	700° K.			200° K.		
Compound	Calculated	A.P.I. data	Stull and Mayfield	Calculated	A.P.I. data	Stull and Mayfield
Methyl-acetylene	24.83	23.58	23.66	28.66	29.69	29.58
1-Butene	38.58	38.71	38.40	50.59	50.62	50.73
n-Octane	85.32	85.66	83.34	111.89	111.8	111.00
Toluene	51.92	51.57	51.17	66.90	66.90	66.86
Methyl-cyclohexane	70.99	72.23	67.07	95.45	96.0	88.49

CONCLUDING REMARKS

This paper proposes group heat capacity equations which may be used to estimate ideal gas heat capacities, that is heat capacities at zero pressure, over the range 300° K. to 1500° K. These are used in the same manner as the liquid group heat capacities also proposed by the authors (3). The method is more rapid than the method of Stull and Mayfield and yields heat capacity as a cubic equation in temperature.

Several methods exist for calculating gas heat capacities at real pressures. Probably the simplest, recommended by both Dobratz (2) and Stull and Mayfield (4), is derived from Berthelot's equation of state and consists of adding the term

$$\frac{81}{32}\frac{P}{P_c}\left(\frac{T_c}{T}\right)^3.$$

NOMENCLATURE

$C_p°$—Ideal gas heat capacity, cal./(deg.) (mole).
p —Pressure, atm.
P_c —Critical pressure, atm.
T —Temperature, ° K.
T_c —Critical temperature, ° K.

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ON THE MEASUREMENT OF THE CONDUCTIVITY OF A FLUID CONTAINED IN A CYLINDRICAL VESSEL[1]

By James R. Wait[2]

ABSTRACT

Analysis is given for the potential problem of two current electrodes located in a homogeneous conducting circular cylinder of finite length. The results lead to a method for determining the conductivity of the cylinder material when the voltage is measured between two potential electrodes.

It is the purpose of this note to outline the basis of a convenient method for measuring the electrical conductivity of a liquid which is contained in an insulating beaker. It will be assumed that the dimensions of the liquid in the beaker are those of a right circular cylinder of radius a and depth c, as illustrated in Fig. 1. Two small electrodes, which subtend an angle $q\pi$ at the

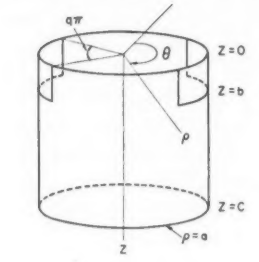

Figure 1

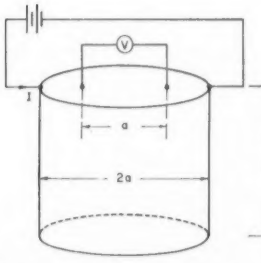

Figure 2

FIG. 1. The cylindrical sample with the appropriate cylindrical co-ordinate system (the current electrodes are not shown to scale; actually b and q are ultimately very small).
FIG. 2. The cylindrical liquid-filled beaker with the final arrangement of the four electrodes.

center, are located at opposite sides of the cylinder and are immersed in the liquid to a depth b. A direct current I is then supplied to the electrodes by a battery or generator and this gives rise to a potential distribution within the

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cylinder. The scheme is to measure the potential difference, V, between two other suitably located electrodes. The transfer conductance, I/V, is then proportional to the conductivity σ of the fluid. The aim of the following analysis is to find the constant of proportionality for a specified arrangement of the four electrodes.

Since the potential is an odd function of θ and is a solution of Laplace's equation, it can be written in the form (1)

$$[1] \qquad \phi = \sum_{n=0}^{\infty} \sum_{\alpha=0}^{\infty} I_n(m_\alpha \rho) \sin n\theta \cos m_\alpha z \, B_{n\alpha}$$

where I_n is a modified Bessel function and $B_{n\alpha}$ is a coefficient which is independent of the cylindrical coordinates (ρ, θ, z). Furthermore, the current normal to the ends of the vessel must be zero and therefore

$$\left(\frac{\partial \phi}{\partial z}\right)_{z=c} = \left(\frac{\partial \phi}{\partial z}\right)_{z=0} = 0$$

which requires

$$[2] \qquad m_\alpha = \alpha\pi/c.$$

Now the radial current density at the walls is given by

$$J_\rho(a) = \left[-\sigma \frac{\partial \phi}{\partial \rho}\right]_{\rho=a} = -\sigma \sum_{\alpha=0}^{\infty} \sum_{n=0}^{\infty} I_n'(m_\alpha a) m_\alpha B_{n\alpha} \sin n\theta \cos m_\alpha z$$

$$[3] \qquad = \sum_{\alpha=0}^{\infty} \sum_{n=0}^{\infty} A_{n\alpha} \sin n\theta \cos m_\alpha z.$$

The factor $A_{n\alpha}$ is obtained by multiplying both sides of equation [3] by $\sin p\theta \cos m_\beta z$ and integrating over half the area of the sides of the vessel.* Since the only current flows through the electrodes and this current is assumed uniform,

$$\text{left side of [3]} = \frac{I}{\pi q a b} \int_{\frac{1}{2}\pi(1-q)}^{\frac{1}{2}\pi(1+q)} \int_0^b \sin p\theta \cos m_\beta z \, d\theta dz$$

$$= \frac{I}{a}\left(\frac{\sin m_\beta b}{m_\beta b}\right)\left(\frac{\sin \frac{1}{2}\pi q p}{\frac{1}{2}\pi q p}\right)\sin \tfrac{1}{2}\pi p$$

and

$$\text{right side of [3]} = \sum_{\alpha=0}^{\infty} \sum_{n=0}^{\infty} \int_0^{\pi} \int_0^{c} A_{n\alpha}(\sin n\theta \sin p\theta)(\cos m_\alpha z \cos m_\beta z) \, d\theta \, dz$$

$$= \frac{\pi c}{4\epsilon_\beta} A_{p\beta} \quad \text{where } \epsilon_\beta = \begin{cases} \frac{1}{2}; \beta = 0, \\ 1; \beta = 1, 2, 3. \ldots \end{cases}$$

It then follows that

$$[4] \qquad \phi(\rho, \theta, z) = -\frac{4I}{\pi c \sigma} \sum_{l=0}^{\infty} \sum_{\alpha=0}^{\infty} \epsilon_\alpha M_{\alpha l} \frac{\sin(2l+1)\theta \cos m_\alpha z \, I_{2l+1}(m_\alpha \rho)}{(m_\alpha a) I_{2l+1}'(m_\alpha a)}$$

where

$$M_{\alpha l} = \frac{\sin(m_\alpha b)}{m_\alpha b} \frac{\sin[\frac{1}{2}\pi q(2l+1)]}{\frac{1}{2}\pi q(2l+1)} \approx 1.$$

This latter approximation is valid for small electrode size.

*p and β, like n and α, are integers.

To obtain the conductivity the dimensions a and c, the current I, and the potential ϕ at some suitable point are measured, and equation [4] is used to find σ. An obvious choice of the point at which to measure the potential is $z = 0, \theta = \pi/2, \rho = a/2$. If $c/a = x$, then from [4]

$$[5] \qquad \phi = \phi(a/2, \pi/2, 0) = -\frac{4I}{\pi\sigma c}\sum_{l=0}^{\infty}\sum_{\alpha=0}^{\infty}\epsilon_\alpha \frac{I_{2l+1}(\alpha\pi/2x)}{(\alpha\pi/x)I'_{2l+1}(\alpha\pi/x)}.$$

The factor

$$T = \frac{4}{\pi}\sum_{l=0}^{\infty}\sum_{\alpha=0}^{\infty}\epsilon_\alpha \frac{I_{2l+1}(\alpha\pi/2x)}{(\alpha\pi/x)I'_{2l+1}(\alpha\pi/x)}$$

has been calculated for two shapes of vessels:

$$x = 1 \text{ gives } T = 0.51034$$

and

$$x = 2 \text{ gives } T = 0.94872.$$

In an actual measurement a cylindrical glass vessel (a beaker) would be chosen and the sample would be placed in it as illustrated in Fig. 2. Two small metallic probes would be arranged so that the difference of potential V between the points $(a/2, 3\pi/2, 0)$ and $(a/2, \pi/2, 0)$ is measured. Using the above results it is apparent that

$$V/I = 2T/\sigma a = 1.0207/\sigma a \text{ for } c/a = 1$$

and

$$V/I = T/\sigma a = 0.9487/\sigma a \text{ for } c/a = 2.$$

The previous results are also applicable to alternating current if the dimensions of the beaker are small compared to the wavelength. This fact has been confirmed experimentally employing audio frequencies.

I would like to thank Mr. D. A. Trumpler for checking the equations and carrying out the computation of T.

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SALT EFFECT IN VAPOR–LIQUID EQUILIBRIUM. PART I[1]

By A. I. Johnson and W. F. Furter

ABSTRACT

Several modifications to the improved recirculation still designed by Othmer are proposed in order to specifically adapt it to the study of salt effect in binary vapor–liquid equilibria.

Isobaric vapor–liquid equilibrium data at one atmosphere pressure are reported for the systems ethanol–water, ethanol–water saturated with mercuric chloride, and ethanol–water saturated with sodium chloride.

INTRODUCTION

Common industrial use is made, as in extractive and azeotropic distillation, of the addition of third components or extracting agents to alter relative volatilities and to alter or eliminate azeotropes, in the interest of facilitating distillation. However, these third components are almost always liquids. Scant attention in the past has been given to the effect of dissolved solid third components. Since a dissolved salt is non-volatile, in order to be effective it would be added to the reflux stream re-entering the column, and would of course flow only downward.

An advantage of the use of solid over liquid third components is that no traces of the extracting agent, being non-volatile, would appear in the overhead product. The method is suited especially to such applications as the production of pharmaceuticals and the preparation of pure monomers for the plastics industry. Recovery of the third component from the bottoms requires not rectification but merely evaporation. Phenol is currently recovered commercially from weak aqueous solutions by a salt process.

Although the exact action of a salt dissolved in a liquid is not certain, it is known that the presence of the salt reduces the volatility of the liquid by lowering its vapor pressure. It is also known that the extent of reduction of volatility depends on the solubility of the salt in the liquid. Hence it would be expected that if the salt were more soluble in the higher boiling, less volatile component of a binary system, then the volatility of this component would be lowered by an amount greater than that of the other. The net result would then be a raising of the ratio of the volatility of the more volatile component to that of the less, or in other words an increase in the relative volatility or ease of separation of the binary system.

Conversely, a salt more soluble in the lower boiling, more volatile component would be expected to reduce the relative volatility of the system since it would depress the vapor pressure of the more volatile component by an amount greater than that of the less.

The various methods of obtaining vapor–liquid equilibrium data are reviewed thoroughly by Robinson and Gilliland (12). Of these methods, the

[1]*Manuscript received August 9, 1956.*
Contribution from the Department of Chemical Engineering, University of Toronto, Toronto 5, Canada.

most popular is the use of a recirculation-type still. Although many varieties of recirculation stills (11, 16) have been devised in order to eliminate shortcomings in the original Othmer design, the improved Othmer still (8) continues to be overwhelmingly chosen, in some modification or other, by the majority of investigators in the field. Othmer's still is noted for simplicity of design and operation, and for giving data of consistent accuracy rapidly.

Although the authors experimented previously with other types of recirculation stills (4), they found the Othmer design to be the most suitably adapted to salt effect studies. This finding is in common with such other salt effect investigators as Reider and Thompson (10), Tursi and Thompson (15), Yamamoto (17), Samaddar (13), Jost (5), and Bogart and Brunjes (2). However, it became evident early in the salt effect investigation that the Othmer design was not ideally suited to this work in its present form. Several modifications to adapt the still specifically to salt effect studies suggested themselves, and these were incorporated for testing into prototypes of the final design described herein.

Although specifically designed for salt effect studies, the described still is not restricted to this application alone. Indeed, it has proved to give accurate data for the ethanol–water system, and should be well suited to liquid third and fourth component studies.

DISCUSSION OF THE APPARATUS

Two main advantages of the design are ease of operation and simplicity. The Othmer design, itself one of the simplest of equilibrium stills, is further simplified by eliminating the intricacies of the constant-volume condensate chamber and the drop counter. The loading port on the side of the pot serves also to hold the pot thermometer with an adaptor, thus eliminating one opening. Since it was desired to design the still to eliminate the salt-clogging problems of other types, the pot drain, which in prototypes was found to trap solid salt and unmixed liquid, was eliminated, both for this reason and for the sake of simplicity.

In salt effect studies analysis of the boiling chamber liquid sample at equilibrium poses a serious problem owing to the presence of salt, although the vapor sample, providing entrainment does not occur, is free of the nonvolatile salt. Some few systems such as those in which one component is an acid may be analyzed by methods such as acid–base titration that are not influenced by the presence of dissolved salt, although salt concentration must be determined in order to convert the composition of a pipetted pot sample to a salt-free basis. However, equilibrium samples of the vast majority of systems must be analyzed by methods, such as specific gravity or refractive index, greatly affected by the presence of a dissolved salt. Tedious calibration or purification methods must then be normally undertaken.

A main feature of the design is the very great ratio of pot volume to condensate chamber volume. This feature simplifies the analysis of samples of equilibrium pot composition containing salt, by making it possible to analyze

the prepared binary charge *before* it is placed in the still and the salt is added. The composition before operation will approach, as this ratio becomes very large, the equilibrium liquid composition. At steady state, only the vapor sample need be analyzed. Incidentally this method also possesses the advantages of producing experimental data rapidly and of giving liquid composition on a salt-free basis directly.

For example, in the case of the system ethanol–water at the point of greatest deviation of vapor composition from liquid composition, and using condensate holdup and pot volumes of 6 and 500 ml. respectively, the greatest error is less than one-half of one mole per cent.

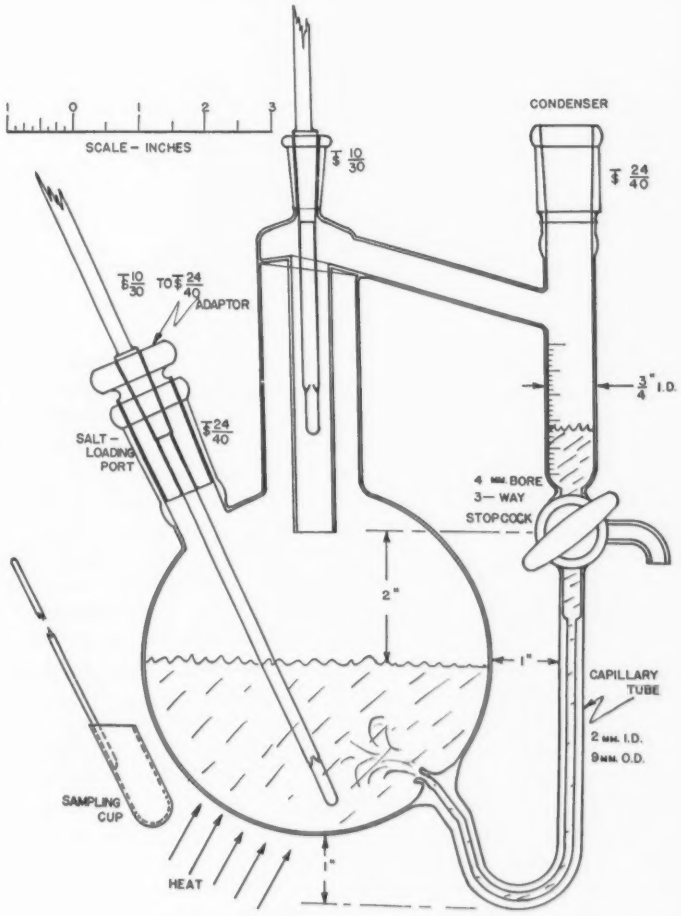

FIG. 1. The vapor–liquid equilibrium still.

If desired, this small error may be eliminated by correcting the binary pot composition, knowing the original composition charged and the volume and measured composition of the equilibrium vapor–condensate sample. The advantage of directly obtained liquid composition on a salt-free basis is retained. The data reported in this paper were corrected by the above method.

A disadvantage of the large boiling chamber lies in the volumes of charge required. Also, this method is not recommended for hydrated or moisture-containing salts in binary systems in which one component is water, since water may be liberated during solution of the salt, causing pot composition to be altered after the sample has been taken.

Fig. 1 shows a scale elevation of the modified still.

The still, the basic component of which is a 1-liter flask, is constructed throughout of Pyrex glass. Precautions against entrainment are taken by including an internal vapor jacket similar to that recommended by Othmer, although its effectiveness has been increased by a considerable lengthening.

Refluxing within the boiling chamber, otherwise a source of error, is completely eliminated by slightly superheating the vapor with a coil of nichrome wire imbedded between two layers of a magnesia–asbestos lagging covering the pot from the liquid level to the top of the neck. While too little superheat permits refluxing, too much tends to cause flashing or complete vaporization of droplets of boiling liquid splashed up on the pot walls, creating a source of error in the steady state vapor sample. A superheat of from two to three degrees is recommended. The ring seal at the top of the neck further ensures against refluxing.

The condenser is mounted in the reflux position to eliminate transport of air into the pot, to reduce structural strains, and to maintain a hot condensate. Fig. 2 is included to show the lagging, the type of condenser found to be the most effective of the several types tested, and the method of heating.

One of the most important modifications found necessary for salt effect work was the inclusion of a *large* port on the side of the boiling flask. It facilitates the loading of salt before a run and also the rapid emptying of the pot after a run by permitting the salt to pour readily without clogging. The large port itself as well as the pot is easier to clean. Access is provided for lowering a cup to sample for salt concentration. Access is also provided to the condensate return nozzle for cleaning and also for loosely packing glass wool into it to prevent the backflow of solid salt crystals, a measure not found to be necessary providing solid salt is not present in too great an excess.

The three-way stopcock joining the condensate chamber to the return line must be located at a level higher than the liquid level in the pot plus capillary effect in order to prevent contamination of the condensate sample by back-mixing of salt-saturated liquid from the pot. The short, curved sampling spout may be rinsed from outside, gently dried by flame, and cooled by an air blast before sampling is done.

The condensate return line, constructed from thick-walled tube for structural strength, is spaced a sufficient distance from the side of the flask to prevent

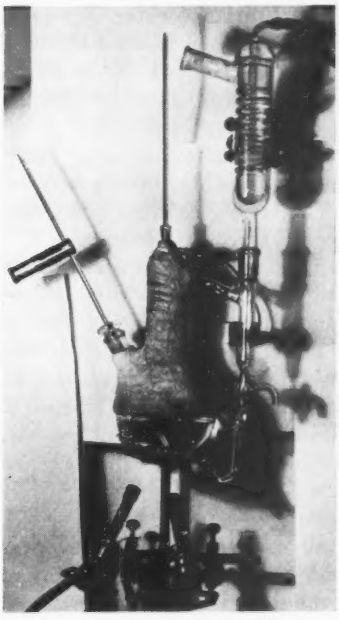

FIG. 2. The still in operation.

boiling in the line caused by heat transfer. It enters the flask near the bottom to provide as much contact as possible of the condensate with the boiling pot contents. The return line dips a short distance below the flask to create a liquid trap to prevent the vapor which forms at the bottom of the pot from passing into the line. Although no difficulty was experienced with the systems tested, any tendency of the returning condensate to vaporize before entering the pot could be resolved by cooling the line with an air blast or water jacket. The nozzle at the end of the return line acts as a jet to aid mixing and to deter the backflow of solid salt. The observed tendency of salt crystals to concentrate around the nozzle ensures rapid saturation of the returning condensate.

The elimination of the pot drain permits heating to be applied off-center, over an area midway between the return line and the liquid level on the far side as shown in Fig. 1, with the following significant advantages: the source of heat is removed from the proximity of the condensate return line, so that special cooling to prevent flashing in this line is not necessary, the returning condensate is allowed to mix better by passing into the pot at a point removed from the most violent boiling, and the immediate contact of unmixed condensate with possibly superheated bubbles at the bottom of the pot is diminished. The latter is a fault for which the conventional Othmer still is often criticized.

For the ethanol–water system a glass col electric heater was found inade-

quate owing to the high latent heat of water. The concentrated flame from two bunsen burners, applied through an asbestos screen shaped to conform with the bottom of the pot and to shield the return line as shown in Fig. 2, was found more suitable. Sensitive control of circulation rate was also possible with this method.

The temperatures of the superheated vapor and the boiling liquid were read with standard taper high quality thermometers which were found to give satisfactory accuracy. The boiling chamber thermometer was calibrated and was read with a telescope to augment accuracy.

An advantage of the modified design arising from the high liquid-to-vapor ratio is an exceedingly rapid rate of approach to steady state. From the mathematical analysis of equilibrium recirculation stills given by Marshall and Pigford (7) and using liquid and condensate volumes of 500 and 6 ml. respectively, 99% equilibrium will be reached on the first filling of the condensate chamber, or at normal circulation rate, in a fraction of a minute. Hence even allowing from 5 to 10 min. of circulation before sampling in order to very closely approach steady state, operation is vastly more rapid than with most currently employed stills.

A main feature of the design is in the flexibility of the condensate chamber volume. For each partially-closed position of the stopcock, there is a specific head of condensate held above the stopcock that may be increased or diminished by adjusting the stopcock. The still is designed in such a manner as to minimize all other sources of holdup to negligible quantities. The condensate return tube is short and of very small bore in order to reduce holdup. Both the ring trap in the top of the pot neck and the vapor transfer tube are slanted to eliminate any holdup at these points. Hence, with the stopcock fully open in the position connecting the condensate chamber to the return line, the still may be initially operated at virtually zero holdup, permitting the correct degree of superheat to be attained and the salt to be dissolved to saturation in the pot. Then the desired condensate level may be established by pinching off the stopcock to the degree necessary to create this level, and the run begun. When a steady state has been reached, the stopcock is rotated to the third position in order to quickly drain the sample through the spout, at the same time cutting off the return line.

The condensate chamber is graduated so that holdup volumes of desired sizes may be established; and also in order that rate of circulation may be measured, thus eliminating the need of a drop-counting device. An in-between position of the stopcock will cut off all three connections to it, causing complete holdup to occur and hence allowing circulation rate to be measured in the calibrated condensate chamber.

The ability to create any desired constant size condensate holdup by adjusting the stopcock gives the still flexibility for use with various systems and methods of sample analysis. The holdup may hence be adjusted for the minimum size of sample required, as recommended by Othmer. Access for cleaning the condensate chamber is available at the condenser joint. Cleaning may be accomplished with a test tube brush when necessary.

The large pot-to-condensate ratio also minimizes certain inherent sources of error in Othmer's design, examples being refluxing and flashing, the dilution of the pot by returning condensate, and the initial unsaturated condition of the returning condensate.

Since boiling appeared to provide adequate agitation, magnetic stirring was not employed.

All joints were lubricated with high-vacuum-type Dow-Corning silicone grease chosen because of its insolubility in the liquids and cleaning fluids used.

It is to be stressed that although a full description of the still has been given in order to facilitate construction and operation, much of the original Othmer design has been retained. A few of the modifications are somewhat similar to those of Smith and Bonner (14), who applied the Othmer still to the study of partially miscible binaries.

The sources of the pure chemicals used to produce the data reported in this paper are as follows. Highly purified absolute alcohol conforming to the specifications of the British Pharmacopoeia was secured from Gooderham and Worts Ltd. The water used was laboratory distilled. Both salts were obtained from British Drug Houses Ltd., the mercuric chloride being of Analar grade and the sodium chloride a certified chemical of not less than 99.5% purity.

PERFORMANCE TESTS

(*a*) *Entrainment*

The maximum possible rate of circulation is governed by the point at which flooding occurs in the mouth of the condenser. At this maximum rate and at rates below, runs were made using the ethanol–water binary system saturated with ammonium chloride. Samples of the condensate were subjected to a Mohr silver nitrate titration and were found to be completely free of chloride ion. A circulation rate of about 20 to 25 ml. per min. was found to give the most satisfactory all-around operation.

(*b*) *Thermometer Calibration*

The pot thermometer was calibrated by boiling various pure chemicals consecutively in the pot and reading the pot thermometer, maintaining a normal slight vapor superheat. A correction chart was plotted.

(*c*) *Time to Reach Steady State*

The system *n*-octane – propionic acid (4) was used for this test, in order to allow a titration-type analysis of the condensate requiring only minute samples so as not to alter the over-all composition in sampling. A composition for which the vapor composition was markedly different from the liquid composition was charged, and time was measured from the formation of the first drop of condensate. Temperature steady state was reached instantaneously as read on the pot thermometer. Operating with zero holdup, composition steady state was also immediate. Operating with a 6 ml. holdup, the size required for specific gravity analysis, steady state to within one per cent was reached in two minutes and to within one-tenth of one per cent in four minutes.

(*d*) *Accuracy*

Fifteen runs were made using the binary system ethanol–water at atmospheric pressure in order to check the accuracy of data obtained from the still.

The results were compared to the best data available, which were obtained in the following manner. A large plot of the ethanol–water data of Carey and Lewis (3), Langdon and Keyes (6), Reider and Thompson (10), Beebe (1), and unpublished data by the authors was made, and the best-fitting line drawn, giving most weight to the data of the first three references above. The ethanol–water data from each of these sources were found to be remarkably consistent with those from the others, with maximum deviations from the best-fitting line being in the order of two- or three-tenths of one per cent.

The data obtained in the 15 runs are reported in Table I.

TABLE I

ETHANOL–WATER, PRESSURE IS 755±2 MM.

Corrected pot temperature, °C.	Mole per cent ethanol	
	In liquid (X)	In vapor (Y)
100.0	0.0	0.0
97.6	0.5	7.4
91.6	3.5	27.7
88.7	5.4	34.9
86.0	9.0	43.7
83.0	18.6	52.1
81.4	32.9	58.1
79.2	54.8	67.4
78.9	64.0	72.0
78.8	76.0	78.8
78.3	87.1	87.5
78.3	91.6	91.4
78.4	95.1	94.6
78.3	98.4	98.0
78.6	100.0	100.0

The comparison between experimental and previously reported data on the ethanol–water system as an accuracy check is shown in Fig. 3. The solid line represents the best data available in the literature, while the points shown as circles are the reported experimental data.

EXPERIMENTAL METHOD

Five hundred milliliters of the desired binary composition was prepared. After a sample was withdrawn for analysis, the mixture was charged to the still along with a quantity of the salt in question and a boiling chip. The still was assembled and heating adjusted for the correct circulation rate. Operation was continued with zero condensate holdup until the correct degree of superheat was attained and until saturation with a slight excess of solid salt was reached, with additions of salt if necessary. The stopcock was then partially pinched off to create a condensate holdup of the size required for a sample. It was carefully adjusted to maintain this level constant. The slight decrease

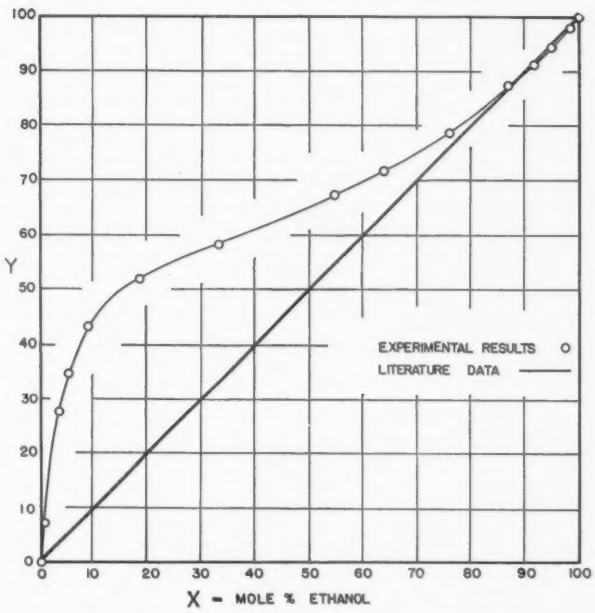

FIG. 3. Ethanol–water at one atmosphere pressure.

caused in pot volume by this buildup further ensures saturation. The still was given from 5 to 10 min. to reach equilibrium. The sampling spout was dried by flame. The sample was quickly withdrawn, stoppered, and placed in a water bath to cool. The condensate sample was taken before operation ceased, in order that errors would not be introduced because of the hot flask jacket continuing to vaporize liquid into the sample after boiling had stopped. For very soluble salts, the volume of charge may be reduced to 300 ml. without materially affecting accuracy.

The ethanol–water system was analyzed by specific gravity using a buoyancy technique employing a sensitive analytical balance. This method required samples 6 ml. in size. The temperatures of the samples at the time of analysis were also measured, in order to calculate the weight per cent ethanol from the tables given in Perry (9). The data were converted to mole per cent.

Should the first few drops of condensate formed refuse to pass through the stopcock when using high concentrations of components with high surface tensions such as water, the situation may be remedied by turning the stopcock to enable suction to be applied at the spout in order to draw liquid from the pot up to the stopcock level, followed by quickly returning the stopcock to its original position. Once circulation starts, this difficulty will not recur.

After the vapor condensate sample had been taken and heating ceased, a pot sample was taken to analyze for salt concentration. At the moment when boiling ceased, the large port on the side of the pot was opened. A brass

sampling cup of previously calibrated volume, as shown in Fig. 1, was lowered into the saturated liquid still at the boiling point. The sample was withdrawn and poured, with repeated interior rinsing with pure water, into a beaker for analysis. Immediately after this, the pot contents was quickly poured into a 1-liter graduate, leaving behind only that excess salt present to ensure saturation, in order to measure the volume of pot charge at saturation. The purpose is to permit calculation of salt concentration in terms of weight per unit of solvent as well as per unit of solution, knowing the volume of salt-free binary mixture initially charged.

EXPERIMENTAL RESULTS

Specific discussion and treatment of salt effect is beyond the scope of this paper. Isobaric rather than isothermal data were obtained because of the industrial significance of the former. The salts sodium chloride and mercuric chloride were chosen for illustration of salt effect because, while sodium chloride is more soluble in boiling water than in boiling ethanol, the reverse is true for mercuric chloride. They were also chosen because neither is hydrated or hygroscopic.

All data are reported on a salt-free basis. Although saturated salt concentrations are not listed, they were determined for each run by silver nitrate titration and will be included in a future publication in the series.

Fig. 4 shows the effect of these salts on the equilibrium curve. Tables II and III list these data.

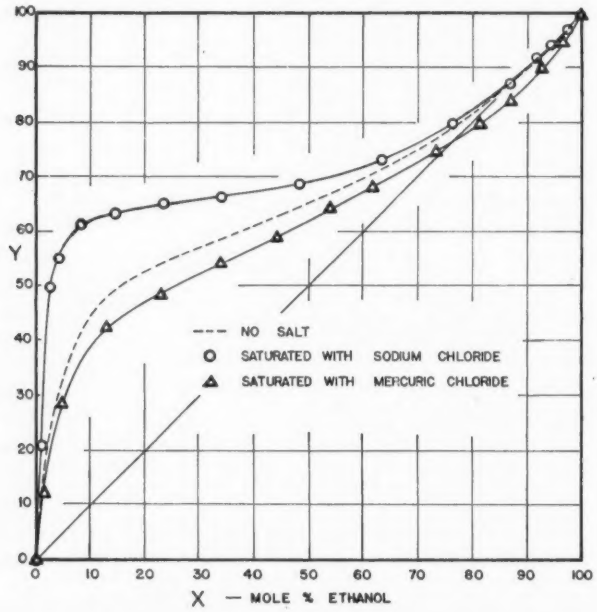

FIG. 4. Vapor–liquid equilibrium curves at one atmosphere.

TABLE II

ETHANOL–WATER SATURATED WITH SODIUM CHLORIDE, PRESSURE IS 755±7 MM.

Corrected pot temperature, °C.	Mole per cent ethanol (salt-free basis)	
	In liquid (X)	In vapor (Y)
108.8	0.0	0.0
101.8	1.1	20.9
88.4	2.5	49.8
85.9	4.2	55.0
82.4	8.0	61.5
80.9	14.6	62.8
80.3	22.9	65.0
80.1	34.0	66.2
79.5	48.0	68.8
78.8	63.4	73.4
78.3	76.4	80.0
77.4	86.9	86.9
78.4	91.7	91.7
77.3	94.5	94.3
77.9	97.3	97.1
77.7	100.0	100.0

TABLE III

ETHANOL–WATER SATURATED WITH MERCURIC CHLORIDE, PRESSURE IS 750±4 MM.

Corrected pot temperature, °C.	Mole per cent ethanol (salt-free basis)	
	In liquid (X)	In vapor (Y)
99.9	0.0	0.0
96.2	1.3	12.2
91.4	4.5	28.3
86.2	12.7	42.6
84.6	22.8	48.2
83.0	33.9	54.3
82.0	44.4	59.0
81.3	54.0	64.6
81.0	61.8	67.9
80.8	73.4	74.9
80.6	81.3	80.0
80.7	87.3	84.4
80.5	92.9	90.1
80.7	96.6	95.0
80.9	100.0	100.0

It is seen that the effects of the two salts on relative volatility are as predicted. The sodium chloride, being more soluble in the less volatile component, increases the relative volatility while the mercuric chloride, being more soluble in the more volatile component, lowers the relative volatility. The sodium chloride, which is very soluble in water but almost insoluble in ethanol, is observed to have little effect on the vapor composition of ethanol-rich mixtures while showing a marked effect towards the water-rich end of the curve. The mercuric chloride, being quite soluble in both components, exerts a more uniform effect across the binary composition range. Sodium chloride is ob-

served to shift the azeotrope composition from 87 to over 90 mole % ethanol while the mercuric chloride transposes it from 87 down to 77%.

Attention is drawn to the self-consistency of the unsmoothed data.

FURTHER MODIFICATIONS

(*a*) If the still were to be used only for systems all of which involved a condensate sample of one single size, the necessity of monitoring the stopcock setting to maintain a constant head could be eliminated by the use of an overflow-type condensate chamber of that size.

(*b*) Fine adjustment of the stopcock setting may be improved by a slight angular reaming of the two ends of the main bore passage of the stopcock rotor.

(*c*) A second method of operating the still, somewhat similar to the method of Smith and Bonner, and as yet untried by the authors, suggests itself. It would be operated at zero holdup, as before, until saturation and superheat were attained, then the stopcock would be pinched off completely to build up a condensate sample of desired size which would then be immediately withdrawn for analysis. The flaw in the method is that as the condensate is building up in size, its composition is differentially changing owing to the changing pot composition caused by this buildup. A mathematical treatment would be required to treat this differential process. However, with a very large pot volume and for very small samples such as required for analysis by titration, the change could be neglected and the condensate analysis left uncorrected.

ACKNOWLEDGMENTS

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THE EXTRACTION OF Th^{230} (IONIUM) FROM A CANADIAN PITCHBLENDE RESIDUE[1]

By A. B. Van Cleave[2] and A. P. Baerg

ABSTRACT

A method from the extraction of ionium (Th^{230}) from a "rare earth residue" fraction accumulated in the radium purification process of Canadian pitchblende has been developed. The efficiency of the process is about 90%. The ratio of Th^{232}/Th^{230} in the concentrate was 2.63.

INTRODUCTION

Ionium (Th^{230}, α active, half life 8.0×10^4 years) is a naturally occurring radionuclide of considerable interest in that, if macroquantities can be isolated, considerable quantities of protactinium-231 (α active, half life 3.4×10^4 years) may be produced by neutron irradiation and subsequent decay of the short-lived Th^{231} to Pa^{231}. The availability of macroquantities of Pa^{231} would make possible a more thorough study of the chemistry of this element. D. F. Peppard and associates (2) have studied the separation of ionium from an aqueous waste resulting from the processing of Belgian Congo pitchblende by the Mallinckrodt Chemical Works.

A rare earth residue that had been accumulated at the Port Hope refinery of Eldorado Mining and Refining Co. Ltd. from the processing of Great Bear Lake pitchblende for radium was thought to contain considerable quantities of ionium. The problem was to establish the amount of ionium in this residue and to devise a scheme for its extraction.

EXPERIMENTAL

1. *Analysis and Ionium Content*

The principal constituents of the residue as determined by chemical and spectrographic tests were barium, lead, iron, cerium, lanthanum, calcium, magnesium, bromide, and carbonate, together with smaller amounts of silver, aluminum, bismuth, copper, nickel, strontium, yttrium, zinc, zirconium, phosphorus, and silicon. The thorium content was too small to be detected spectrographically. The large amounts of lead and barium present made it necessary to employ large volumes of acids (such as nitric and hydrochloric) to obtain complete solution of the sample. Hot concentrated nitric acid 0.01 molar in ammonium silicofluoride was the more effective solvent, dissolving all but a small amount of siliceous residue. This residue, when dissolved in hydrofluoric acid, was found to contain less than one per cent of the total alpha activity.

By means of an alpha energy analysis, it was established that the sample

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contained approximately 20 mgm. of Th^{230} per kgm. of the rare earth residue. In a freshly isolated portion of thorium only about 14% of the alpha activity was due to Th^{230}, the remainder of the alpha activity being due to 18.6 day Th^{227}. All of the daughters of Th^{227} were found to be present in the original sample. The presence of Th^{227} indicated that the residue also contained some Ac^{227}.

2. Extraction Procedure

Since excessively large volumes of acids were required to dissolve the residue completely, a procedure involving solvent extraction from a slurry was developed. At least 90% of the ionium could be extracted from the residue as follows:

A 250-gm. sample of residue was treated with 300 ml. of conc. nitric acid.* The partially dissolved sample was evaporated to dryness and baked at 400° C. for several hours.† The dried sample was taken up in 300 ml. of 4 *N* nitric acid and the resulting slurry was stirred and warmed for eight hours and then let stand for several days with only occasional stirring. During this period, sufficient aluminum nitrate hexahydrate (about ½ lb.) was added to saturate the solution.

The slurry was agitated for 10 min. with 200 ml. of mesityl oxide (1), let stand until the layers separated, after which the organic phase was removed and backwashed with water. The slurry was given a second extraction with the recovered mesityl oxide. The backwashings were combined and the volume of solution was reduced by precipitation with ammonia followed by dissolution of the precipitate in 2 *N* nitric acid.

3. Purification of the Ionium Extract

(a) Oxalate Precipitation

Thorium is separated from most elements other than rare earths by oxalate precipitation in acid solution (3). The precipitate formed by adding saturated oxalic acid to the nitric acid solution of thorium extract was washed and dissolved in concentrated nitric acid plus 30% hydrogen peroxide to destroy the oxalate. The thorium was reprecipitated as the hydroxide with ammonia and redissolved in approximately 6 *N* nitric acid.

(b) Iodate Precipitation

Thorium can be separated from most elements except zirconium, titanium, and cerium IV by an iodate precipitation from a nitric acid solution (3). The precipitation of cerium IV can be minimized by reducing it to cerium III with hydrogen peroxide. After adding hydrogen peroxide to the solution, a standard iodate precipitation was performed, followed by dissolution of the precipitate in concentrated nitric acid plus 30% hydrogen peroxide.

**Conc. nitric acid was used to rid the solution of bromide, which was found to cause excessive polymerization of the organic solvent (mesityl oxide).*

†Baked samples caused less polymerization of the mesityl oxide and resulted in a more satisfactory separation of the layers in the solvent extraction step.

(*c*) *Ion Exchange Purification*

It appeared that even after three successive alternate precipitations as oxalate and iodate, there was still some impurity in the ionium concentrate since the precipitate resulting from the addition of ammonia was difficult to dissolve. A final purification was made using a Dowex-50 cation exchange resin.

The ionium concentrates which were accumulated from about 700 gm. of the rare earth residue, and which had undergone at least one oxalate and one iodate precipitation, were placed on a column of Dowex-50 resin (200–500 mesh size) in the hydrogen form and eluted with 4 *N* nitric acid solution. The resin column was about 10 cm. in depth and 1.2 cm. in diameter. The flow rate was 0.66 cm./min.

The eluant was collected in 10-ml. fractions. The first two fractions showed considerable alpha activity in the solution both before and after precipitation with ammonia. This alpha activity was due to Ra^{223} and other disintegration products of Th^{227}. White precipitates formed in the first two eluant fractions on the addition of ammonia. The main constituents in the precipitate from fraction 1 were determined by spectrographic analysis to be aluminum, bismuth, iron, calcium, lead, silicon, and phosphorus (the latter probably as phosphate). The presence of phosphate would explain why the precipitate formed on addition of ammonia to the ionium concentrate was sometimes difficult to dissolve. Precipitates of silica were frequently encountered.

The next five 10-ml. portions of 4 *N* nitric acid eluant contained progressively smaller amounts of alpha activity and also gave progressively smaller amounts of a slightly orange-colored hydroxide on the addition of ammonia. The hydroxide precipitate from fraction 4 was examined spectrographically, the main constituents being bismuth, cerium, lanthanum, and silica. It was evident that the iodate precipitation had not been completely effective in separating lanthanide elements from thorium. The eighth and ninth 10-ml. portions of eluant gave no visible precipitates on the addition of ammonia.

The eluant was then changed to 1.25 *M* $NaHSO_4$ solution to strip the thorium from the resin (5). Virtually all of the ionium concentrate was eluted in the first 60-ml. fraction. The thorium was precipitated with 5 *N* sodium hydroxide solution, collected, and dissolved in nitric acid. The concentrate was then subjected to three successive precipitations with ammonia, after which the precipitate was washed with 5% ammonium chloride solution containing dilute ammonia and dissolved in nitric acid. This procedure was adopted to free the concentrate of sodium ion.

(*d*) *Analysis of the Concentrate*

The total amount of Th^{230} in the concentrate from 700 gm. of residue was determined to be 12.3 mgm. by measuring the Th^{230} alpha disintegration rate in an aliquot of the solution with an alpha energy analyzer. The efficiency of the extraction process outlined above was thus approximately 90%.

The isotopic purity of the concentrate was determined by precipitating a portion as iodate using the conditions outlined in section *3(b)*. The iodate in a portion of the precipitate was determined by the standard iodometric method (4). The Th^{230} content of an aliquot of the titrated solution was then determined using the alpha energy analyzer. Assuming that the iodate precipitate was $Th(IO_3)_4$, the ratio Th^{232}/Th^{230} in the final concentrate was calculated to be 2.63. The whole sample of thorium concentrate therefore contained 12.3 mgm. of Th^{230} and 32.4 mgm. of Th^{232}.

4. Discussion

The extraction procedure and results reported above are of particular interest from several standpoints. The "rare earth residue" yields an ionium concentrate of higher isotopic purity than others which have been reported (2). The method, with minor modifications, should be applicable to large scale extraction of ionium from this or other solid residues. The main differences between this method and that previously published (2) are the solvent extraction from slurry step and the inclusion of a final purification involving ion exchange.

ACKNOWLEDGMENT

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ALGEBRAIC REPRESENTATION OF VAPOR-LIQUID EQUILIBRIUM DATA[1]

By A. I. Johnson and W. F. Furter

ABSTRACT

The relative merits of algebraic vs. thermodynamic correlations of non-ideal vapor–liquid binary equilibrium data are discussed. A survey of previous attempts at algebraic representation is given. A rapid and easily handled algebraic representation is proposed that meets the criteria for such expressions, containing only two empirical constants both readily evaluated from a simple straight-line plot, relating x and y directly, and permitting the calculation of azeotropic compositions. Its merit lies in its simplicity.

The equation was subjected to a critical test with 57 different binary systems. It was found to represent, in general, systems containing no strongly polar or long-chained components and, in the more limited case, systems in which both components are polar but are of somewhat similar molecular types and sizes, and degrees and types of polarity. The accuracy was better than one per cent over the ranges for which data were available. For these types of systems, the equation is concluded to be useful from a practical standpoint for engineering calculations such as the calculation of azeotrope compositions, and for representing experimental, non-ideal vapor–liquid equilibrium data within the described limitations.

INTRODUCTION

Although non-ideal vapor–liquid equilibrium data are normally tested for consistency and correlated by various thermodynamic methods, there is much to be said for the use of a quick and simple algebraic method. Thermodynamic correlations such as those of Margules (14), Van Laar (14), Redlich and Kister (12), and Scatchard (14) emphasize the theoretical aspect but often require involved and time-consuming calculations from data which may not always be readily available. They resort to derived functions such as activity coefficients and ratios of activity coefficients, rather than to a direct relation between x and y.

On theoretical grounds, it appears that no simple algebraic relation between x and y can apply to every system over its entire range. However, it has been found that some algebraic correlations will hold over the major portion of the composition ranges of a good many non-ideal systems and are applicable over certain portions of many others. For practical purposes, a rapid and easily handled equation that would permit a simple algebraic treatment rather than the somewhat tedious and often complicated calculations of the more elegant theoretical methods would be a desirable tool for the engineer. The principal uses of such an equation would be the smoothing of experimental data, the testing of data for self-consistency, interpolation, and the prediction of azeotropic compositions.

To be of practical significance, an algebraic method should meet certain criteria. It should primarily present accurate correlations of as many systems

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over as wide a composition range as possible. The equation should relate x and y directly. It should have as few empirical constants as possible. These constants should be capable of ready and quick evaluation. A simple straight-line plot is desirable.

Several investigators have attempted to develop a simple but useful algebraic correlation. A summary of their findings follows.

Clark (3) suggested representing x–y data by two hyperbolas:

$$\frac{y}{1-y} = a\left(\frac{x}{1-x}\right)+b,$$

$$\frac{1-y}{y} = a'\left(\frac{1-x}{x}\right)+b'.$$

His correlation, however, requires two lines and hence four constants per system, but permits a simple straight-line plot. Unfortunately, the molar ratios taper to indeterminate quantities or infinity at the ends.

A trial-and-error method was developed by Kretschmer and Wiebe (9) using the relation

$$\alpha = \frac{A-Bx}{(x+c)(1-2C+Cx)}.$$

By trial and error, various values of C are tested until a straight line is obtained. However, the relation does not have the desired simplicity.

Prahl (11) and later Gilmont (5, 6) using the equation

$$y = \frac{Cx(A-x)}{Cx(A-x)+(1-x)(B+x)}$$

were able to evaluate their three empirical constants by a graphical method requiring one experimental point of known accuracy. Prahl found that many systems could be represented by one straight line covering the entire composition range while practically any system could be covered by two or sometimes three straight lines, and hence requiring three, six, or nine constants per system. He pointed out that algebraic correlations are especially valuable for systems in which association in the gaseous phase exists.

Eshaya (4) studied the possibility of representing vapor–liquid equilibrium data by a simple power series of the form

$$y = Ax+Bx^2+Cx^3+Dx^4+\ldots.$$

He found that normally three but sometimes four terms were necessary for accuracy to within a few per cent.

All of the above correlations may be criticized for the reason that in none of them are the constants as capable of quick and ready evaluation as might be desired.

Yu and Coull (16) using an expression of the form

$$\frac{y}{1-y} = A\left(\frac{x}{1-x}\right)^B$$

gained the advantage of simplicity in the evaluation of the empirical constants. A straight line or lines were proposed to result from a log–log plot of the molar ratios. However, the fact that molar ratios are involved makes the equation invalid for dilute solutions. They tested their equation successfully on 10 moderately non-ideal systems, noting better accuracy with one system than the Eshaya power series with three terms, and claiming accuracy to within two per cent for the composition range of 0.04 to 0.96 mole fraction.

Perhaps the most interesting work in this field has been done by Hirata (7) and later by Othmer (10). Hirata found that most equilibrium curves could be represented by three straight lines. In a plot similar to that used by Yu and Coull, namely, $y/(1-y)$ plotted against $x/(1-x)$ on log–log paper, over the central portion of the composition range a straight line of slope characteristic to the particular system would result, while both ends of the curve for all systems could be represented by straight lines of slope unity. This method of correlation may be criticized for the abrupt changes of slope occurring at the junctions of these three lines, since the correlation may only approximate and never truly represent natural data which do not tend to exhibit such sharp changes.

In this paper, an algebraic correlation will be proposed that is simple and fast to use. It has been found to approximate closely many non-ideal systems by a single straight line involving only two empirical constants, both of which can be quickly and readily obtained from the slope and intercept of the straight line. It relates x and y directly, and permits the calculation of azeotropic compositions. It has been subjected to a critical and comprehensive test in an effort to investigate its degree of applicability to various types of non-ideal binary systems, with a view to predicting its limitations and applications in practice.

THE CORRELATION

For an ideal system, α is constant, and

$$y = \frac{\alpha x}{1+(\alpha-1)x}. \qquad [1]$$

The relative volatility α for a non-ideal system is defined as

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2}. \qquad [2]$$

The Raoult Law activity coefficient, or deviation factor from ideality in a non-ideal system, is defined as

$$y_i/x_i = \frac{\gamma_i P_i^0}{P_T} \qquad [2a]$$

and hence the expression for relative volatility in a non-ideal system may be written as

$$\alpha_{12} = \frac{\gamma_1 P_1^0}{\gamma_2 P_2^0}$$

which, after taking logarithms and differentiating, becomes

$$d \log \alpha_{12} = d \log \gamma_1 - d \log \gamma_2. \quad [3]$$

The Gibbs-Duhem equation may be written

$$x_1 \, d \log \gamma_1 + x_2 \, d \log \gamma_2 = 0. \quad [4]$$

Combining equations [3] and [4], the following equation is obtained:

$$d \log \gamma_2 = -x_1 \, d \log \alpha_{12}. \quad [5]$$

Since $\gamma_2 = y_2 P_T / x_2 P_2^\circ$ and $x_2 = 1 - x_1$ and $y_2 = 1 - y_1$, then equation [5] may be written

$$d \log y_1/x_1 = x_1 \, d \log \alpha_{12} \quad \text{or}$$

$$\log \alpha_{12} = \int_0^{x_1} \frac{1}{x_1} \, d \log \frac{y_1}{x_1} + C. \quad [6]$$

From equation [6] several conclusions may be drawn. For non-ideal systems, α is seen to be not a constant but rather a function of composition. Equation [6] also indicates that a correlation should be sought through α. Equations [1] to [6] illustrate the theoretical approach attempted. The complexity of equation [6] renders it unsuitable for the rapid and simple engineering correlation desired, justifying further simplification.

Equation [6] may be expressed in the simpler and more general form

$$\alpha_{12} = A x_1^B \quad [7]$$

where A and B, although actually functions of composition, may in the simplest case be considered as constants. The conditions under which A and B may be assumed to approximate constants are discussed in a later section.

To obtain a straight-line plot and to evaluate the two empirical constants A and B, α_{21} is calculated for each experimental point using equation [2]. From equation [7] it is seen that a plot of log α vs. log x will produce a straight line if A and B are constant. From this plot, A and B are evaluated from the intercept and slope respectively of the resulting best straight line drawn through the points. The equation of this straight line will be seen to be

$$\log \alpha_{21} = B \log x_2 + \log A. \quad [8]$$

Hence the proposed algebraic correlation takes the form

$$y/(1-y) = A \; x^{B+1}/(1-x). \quad [9]$$

Although exhibiting certain similarities to the expressions of Clark, Hirata, Othmer[4] and Yu and Coull the proposed equation possesses certain advantages in simplicity of application and in evaluation of the constants. For the systems to which it is applicable, it was found to give accuracy to the order of less than one per cent deviation, using only two empirical constants and a single straight line to represent these systems over all but a small fraction of their composition ranges.

Comparing equation [9] to that of Yu and Coull, it will be seen that the difference lies in the fact that only the numerator is raised to a constant power rather than the entire mole ratio of x. The accuracy is better than that reported by Yu and Coull and is observed to be applicable to higher values of x than their 0.96 limiting value.

Equation [9] was found to hold over a wider composition range than the middle straight line of the trio of lines used by Hirata and Othmer.

DISCUSSION

From the nature of the equation, it can be seen that a straight line on a log–log plot cannot represent a system over its entire composition range, since it can be proved that the relative volatility for dilute solutions approaches unity:

$$\alpha = \frac{y(1-x)}{x(1-y)}$$

$$\lim_{x \to 0} \alpha = \frac{0}{0}$$

and is indeterminate. Applying l'Hôpital's Rule,

$$\lim_{x \to 0} \alpha = 1.$$

Similarly,

$$\lim_{x \to 1} \alpha = 1.$$

Hence, at both ends of the curve, the slope of the straight line must approach certain fixed slopes in the limit

$$\alpha = Ax^B.$$

Taking logs, $B = (\log \alpha - \log A)/\log x$ where B is the slope of the log α vs. log x curve, and

$$\lim_{x \to 0} B = 0 \qquad \text{and} \lim_{x \to 1} B = \infty.$$

In a manner similar to the Hirata and Othmer expression, the proposed equation in the dilute region below 0.04 mole fraction could be represented by a second straight line of slope zero, should it be desired to extend the correlation into this dilute region. However, the same criticism of the abrupt change in slope as for the Hirata method would then be incurred.

However, the merit of an engineering correlation lies in its usefulness and applicability rather than in its rigorousness. Although it has been proved that no system can be represented over its entire composition range by a straight line on a plot of the type proposed, in practice it has been found that over the entire composition range excepting a few per cent at either end, many systems indeed tend to follow a straight line quite precisely. It is over this central portion of the composition range that most engineering calculations are made. It was found in practice, that because of the power nature

of the equation, the limiting conditions for dilute solutions did not begin to influence the log α vs. log x curve for systems where a straight line was observed until very near the ends of the curve, especially at the high end.

It will be noted that the numerical value of the empirical constant B is in effect a measure of the non-ideality of the system. For an ideal system, B will be zero and equation [9] will reduce to equation [1], the Fenske equation for ideal systems.

Azeotropic composition may be calculated from equation [7]. Since at the azeotropic composition $x = y$ and hence $\alpha = 1$, then the composition at which the azeotrope occurs is $x = (1/A)^{1/B}$. Thus, azeotrope compositions may be predicted from a knowledge of the two empirical constants alone.

OBSERVATIONS

In reviewing the literature on previously-proposed algebraic correlations, it was noticed that none of the correlations had been really thoroughly tested to assess their worth. It was decided to put the equation to a comprehensive test to examine algebraic methods in general, to examine critically the conclusions drawn about its applicability to different types of systems, and to furnish tables of useful data. A total of 67 systems were chosen from the literature. The sources of data were mainly the books by Robinson and Gilliland (13), Chu (2), and Rose (15). A sharp distinction was found to exist between systems containing and systems not containing strongly polar compounds.

The equation was tested on each system in the following manner. For each point, α was calculated and plotted against x on log–log graph paper. The best straight line was drawn through the points. From it the constants A and B were evaluated. Then all the original values of x were substituted into the equation and y was calculated for each point. The numerical difference between the observed and calculated value of y for each point was obtained, and the arithmetic average of these deviations for the entire system was calculated. It is to be stressed that the numerical values of the deviations regardless of sign were averaged, so that a positive and a negative deviation would not tend to cancel out and create an erroneous or exaggerated impression of the ability of the equation to represent the data.

From a review of the systems tested, the following observations were made:

(*a*) Of the 67 systems selected, 10 were initially rejected without testing because of obvious scattering of experimental data or paucity of data. Of the 57 systems tested with the correlation, 37 could be classed as containing one or more strongly polar components, such as alcohols, organic acids, water, aldehydes, ketones, alkyl halides, or long-chain sulphides or cyanides. The remaining 20 could be classed as containing no strongly polar components, examples being short-chain halides, esters, and sulphides; saturated and unsaturated hydrocarbons; ethers; and aromatics.

(*b*) Of the 37 systems falling into the classification of having one or more strongly polar components, only 10 were found to be capable of representation

to within one per cent. In these 10 systems, both components are observed to be of somewhat similar sizes to each other and to have generally short molecules. Tables I and II list these systems.

TABLE I

SYSTEMS CONTAINING ONE OR MORE STRONGLY POLAR COMPONENTS, TESTED AND FOUND NOT TO GIVE ACCURATE REPRESENTATION. IN ALL CASES PRESSURE IS CONSTANT AT ONE ATMOSPHERE

No.	System		Ref.
	Component No. 1	Component No. 2	
1	Acetic acid	Acetic anhydride	2, 13
2	Acetic acid	Acetone	2, 13
3	Acetic acid	Ethyl acetate	2, 13
4	Acetone	Carbon tetrachloride	15
5	Acetone	Ethanol	2
6	Acetone	Methanol	2
7	Acetone	Water	2, 13
8	Acetonitrile	Water	13
9	Benzene	Acetic acid	2
10	Benzene	Ethylene chlorohydrin	2, 13
11	*n*-Butanol	*n*-Butyl acetate	2, 13
12	Carbon disulphide	Acetone	2
13	*cis*-Dichloroethylene	Methylal	15
14	Ethanol	Ethyl acetate	2, 13
15	Ethanol	Water	13
16	Ethylene chlorohydrin	Toluene	2, 13
17	*n*-Heptane	Propionic acid	1
18	*n*-Hexane	Propionic acid	1
19	Methanol	Water	2, 13
20	Methyl ethyl ketone	*n*-Heptane	2
21	*n*-Octane	Propionic acid	8
22	*n*-Pentane	Propionic acid	1
23	Isopropanol	Water	2
24	*n*-Propanol	Water	2
25	Propionic acid	*n*-Decane	1
26	Propionic acid	Water	8
27	Water	Isobutanol	13

TABLE II

POLAR SYSTEMS REPRESENTABLE BY THE CORRELATION

No.	System		Ref.	Pressure, atm.	*A*	*B*	Average deviation, *y*, mole fr.
	Component No. 1	Component No. 2					
28	Acetic acid	Water	2, 13	760 mm.	1.70	−0.088	0.009
			2, 13	500 mm.	1.74	−0.029	0.005
			2, 13	250 mm.	1.29	−0.158	0.007
			2, 13	125 mm.	1.21	−0.160	0.004
29	Acetone	*n*-Butanol	2, 13	1	18.1	0.223	0.004
30	Acetone	Chloroform	2	1	1.94	0.583	0.005
31	Acetone	Trichloroethylene	13	1	10.2	0.377	0.006
32	Isobutanol	Ethylene chlorohydrin	2, 13	1	1.84	−0.062	0.003
33	*n*-Butanol	Ethylene chlorohydrin	2, 13	1	1.40	−0.097	0.005
34	Ethylene oxide	Acetaldehyde	15	1	1.60	0.056	0.003
35	Phenol	*m*-Cresol	2, 13	1	1.62	−0.106	0.006
36	Phenol	*o*-Cresol	2, 13	1	1.28	−0.044	0.007
37	Water	Formic acid	2, 13	1	2.72	1.215	0.006

(*c*) Of the 20 systems falling into the classification of having no strongly polar components, all 20 were capable of faithful representation by the equation, and all but one to better than one per cent accuracy. Over the ranges of data given in the literature, these latter systems could be represented by a single straight line on a log–log plot, as is verified by the average deviations shown in Table III. It is to be pointed out that some of the pre-

TABLE III

NON-POLAR SYSTEMS

No.	System		Ref.	Pressure, atm.	*A*	*B*	Average deviation *y*, mole fr.
	Component No. 1	Component No. 2					
38	Benzene	Cyclohexene	2	1	0.899	−0.246	0.004
39	Benzene	Ethylene dichloride	13	760 mm.	1.08	0.000	0.003
			13	400 mm.	1.12	0.000	0.003
			13	200 mm.	1.15	0.000	0.004
			13	100 mm.	1.10	−0.056	0.008
40	Benzene	*n*-Hexane	2	1	1.13	−0.322	0.013
41	Benzene	Toluene	2	1	2.50	0.000	0.006
42	Carbon disulphide	Carbon tetrachloride	2, 13	1	2.44	−0.092	0.006
43	Carbon tetrachloride	Benzene	2	1	1.02	−0.105	0.002
44	Carbon tetrachloride	Ethyl acetate	2	1	1.10	0.000	0.008
45	Carbon tetrachloride	Toluene	2	1	2.40	0.000	0.002
46	Chlorobenzene	Ethylbenzene	15	1	1.10	−0.004	0.001
47	Chloroform	Benzene	2	1	2.30	0.260	0.005
48	Cyclohexane	2,2,3-Trimethylbutane	2, 13	1	0.886	−0.187	0.002
49	Ethylene dichloride	Toluene	2	1	2.32	0.041	0.002
50	*cis*-Dichloroethylene	Isopropyl ether	15	1	1.48	0.166	0.004
51	Ethyl bromide	Benzene	2, 13	1	4.62	0.139	0.005
52	Ethyl ether	Carbon tetrachloride	2, 13	1	4.38	0.000	0.002
53	*n*-Heptane	Toluene	2, 13	1	1.14	−0.233	0.005
54	*n*-Octane	Toluene	2, 13	1	1.20	−0.312	0.009
55	Trichloroethylene	Tetrachloroethylene	15	1	3.14	0.045	0.003
56	2,2,3-Trimethylbutane	Benzene	2, 13	1	0.697	−0.418	0.009
57	2,2,4-Trimethylpentane	Methyl cyclohexane	2	1	1.00	−0.069	0.005

viously-reported algebraic correlations require two and even three straight lines per system, requiring their equations in reality to have not two but four or six constants. It was found that only one straight line was required to represent the systems in all cases by the proposed correlation, making it strictly a two-constant equation.

(*d*) In general, the correlation was found to represent accurately systems described in (*c*) above for values of x from about 0.04 to well beyond 0.98 mole fraction, and that the limiting end effects derived in the Discussion section did not materially influence the data within this range.

(*e*) For systems consisting of two polar components, such as water with members of the alcohol series and water with the organic acids, the corre-

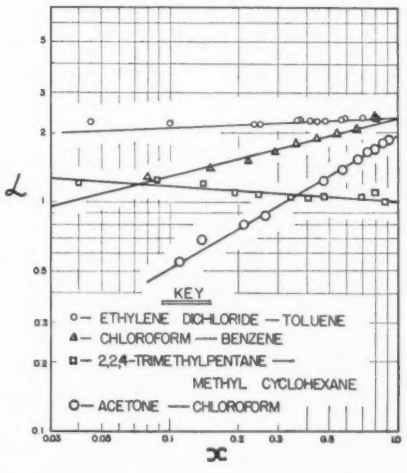
lation was observed to work best with the lowest members of the series and to become progressively less representative as the series was ascended.

(*f*) Systems such as octane–toluene consisting of one compact molecule and one long-chain molecule exhibited deviations from the simple assumption of A and B remaining constant, giving a slight curve on the log–log plot rather than a straight line, although the best straight line was still able to represent the data fairly closely.

(*g*) Insufficient data were available to come to any conclusion on the effects of branched- as opposed to straight-chain molecules of the same molecular weight.

Examples

Fig. 1 below illustrates systems for which the correlation is applicable, while Fig. 2 is included to show the type of curves observed for systems that cannot be correlated by assuming A and B to be constant. In all examples, pressure is atmospheric.



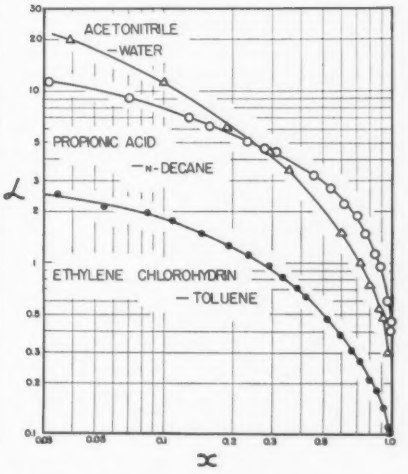


FIG. 1. An illustration of systems representable by the proposed correlation.
FIG. 2. An illustration showing the types of deviations observed for systems to which the correlation may not be accurately applied.

RESULTS

The method of testing has already been described. It must be pointed out that x and y are defined, not as the mole fraction of the more volatile component, but as the mole fraction of component No. 1, as listed in the tables, in order to avoid ambiguity in the values of the empirical constants. Hence, in azeotropic systems this means that α as defined here will have values of less than unity over a portion of the concentration range. The values of y were calculated for each value of x in all systems and the arithmetic average of the numerical deviations regardless of sign are reported. When the log α

vs. log x plot is made, the data are seen to deviate from the straight-line relationship towards both ends. Owing to the power nature of the equation, in drawing the best straight line more weight must be given to the points in the central portion of the x range than the points towards the ends. It was found in practice that points at the ends of the curve located considerably distant from the best straight line did not deviate nearly as much from the equation as would appear at first glance.

It is to be stressed that the calculated deviations reported in the tables comprise not only the deviation of the system from the proposed correlation, but also the experimental error and scattering of the data, which in many cases had not been smoothed. Also it is to be noted that no points in any of the systems tested were rejected, even if they were apparently inconsistent.

It will be noted that for a few of the systems in Table III B has a value of zero. This means that the systems in which this occurs act ideally and have a constant relative volatility.

The constants reported in Tables II and III are calculated from the data given in the references indicated and are only as good as the quantity and quality of the data. For some systems only a few points exist in the references and from these A and B were calculated. When better data are reported in future literature, A and B may then be recalculated to more accurate values.

DISCUSSION OF RESULTS

The correlation, as expected, was more applicable to systems in which neither component was strongly polar than to systems containing highly polar components. In the former, the relative volatility would be expected to be a comparatively simple function of composition, since little association occurs in either phase to make molecular relationships more complex. Similarly, the equation applied best to systems in which molecules of both components were compact and of somewhat similar sizes, presumably since mobility restrictions due to tangling would be minimized or at least be similar for both components.

It is proposed that the explanation for the correlation not applying well to systems in which one component was strongly polar and the other not is that although the molecular state of the non-polar component would be little affected by changing composition, on the other hand as the concentration of the polar component increased and polar molecules became closer to each other, molecular association in the polar component due to hydrogen bonding or other attractive forces would rapidly increase. Hence, the volatilities of the two components would each vary in a different manner to that of the other, with changing concentration. The relative volatility would no longer be a comparatively simple function of composition, and A and B could not with the same justification be expected to remain relatively constant. Similarly, systems composed of a component with compact, spherical molecules such as an aromatic and a component with long linear molecules such as a long-chain alkane would act in a manner similar to the preceding case. An

increase in the concentration of the long-chain component would result in a much sharper change in its mobility and hence volatility than in that of the compact molecule, owing to the occurrence of chain tangling among molecules of the linear component. A parallel explanation accounts for the non-applicability of the correlation to systems in which both components are polar, and where the two components have molecules of greatly differing size, mobility, or polarity from each other.

The deviation was observed to be greatest in binary systems of a single polar component where the polar molecule was smallest. For instance, in systems where the polar component was an alcohol or organic acid, the deviation was greatest for the lowest members of the homologous series, decreasing with increasing molecular weight. The proposed reason is that since each polar molecule has only one polar group, a net reduction in the polarity of the polar component occurs as the series is ascended owing to a decrease in both the number of polar groups per unit weight and the mobility.

The equation was found to apply also in the more limited case of systems in which both components are strongly polar, and in which both are of somewhat similar molecular sizes and shapes, and of similar degrees and types of polarity. In a system such as methanol–water, for instance, it is probable that a molecule of methanol would have little to choose between hydrogen bonding with a molecule of water or with another molecule of methanol. These deviations, as might be expected, became more pronounced in systems such as alcohol–water or organic acid–water as the homologous series was ascended.

Systems with molecules containing polar groups other than OH groups, such as halides and sulphides, worked best when the molecules were short- rather than long-chained, probably because in effect the degree of polarity was less in the more spherical molecules.

SAMPLE CALCULATION

System: Cyclohexane–2,2,3-trimethylbutane.

Calculations: All x and y values are mole fraction cyclohexane.

Given data		Calculations				Numerical deviation of y
x	y	α	A	B	Calc. y	
0.042	0.066	1.61	0.886	−0.187	0.066	0.000
0.118	0.149	1.31	,,	,,	0.150	0.001
0.225	0.255	1.18	,,	,,	0.254	0.001
0.279	0.306	1.14	,,	,,	0.304	0.002
0.379	0.396	1.08	,,	,,	0.393	0.003
0.435	0.443	1.03	,,	,,	0.443	0.000
0.484	0.491	1.03	,,	,,	0.487	0.004
0.517	0.518	1.00	,,	,,	0.518	0.000
0.522	0.522	1.00	,,	,,	0.522	0.000
0.665	0.654	0.95	,,	,,	0.654	0.000
0.757	0.748	0.95	,,	,,	0.745	0.003
0.834	0.823	0.93	,,	,,	0.822	0.001
0.871	0.860	0.91	,,	,,	0.860	0.000
0.912	0.900	0.87	,,	,,	0.902	0.002
0.940	0.927	0.81	,,	,,	0.933	0.006
0.963	0.952	0.76	,,	,,	0.958	0.006

Average numerical deviation = 0.002 mole fraction cyclohexane. Values of α were calculated from equation [2] and A and B were evaluated from Fig. 3. The values of y were recalculated from equation [9] and the deviations

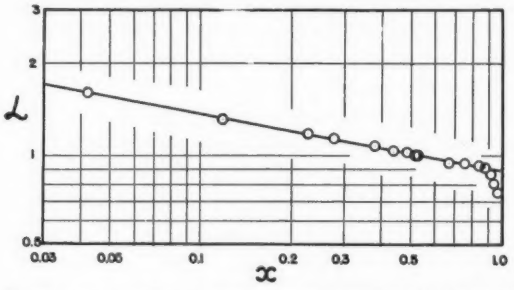


FIG. 3. Plot of log α vs. log x for the system cyclohexane–2,2,3-trimethylbutane.

listed. The system was chosen for illustration because it is azeotropic and also because it exhibits a deviation from the straight line above 0.90 mole fraction as may be seen in Fig. 3, which, however, is minimized by the nature of the equation and still permits good representation of these points by the equation.

CONCLUSIONS

The proposed algebraic correlation, after comprehensive testing, was found to represent, in general, binary systems containing no highly polar compounds, and in the more limited case systems of polar compounds where both compounds comprising the system were of roughly similar sizes, molecular configurations, and type of polarity. For the systems to which the correlation is representative, a considerable portion of even the small deviations reported may be attributable to experimental error in the data. Over the portion of the composition range excluding the very dilute regions, representation adequately accurate for engineering purposes and in most cases to better than one per cent was obtained. The equation contains only two empirical constants, both readily and easily evaluated from a simple straight-line plot. A second line of slope zero may be used to extend the correlation into the dilute region below 0.04 mole fraction if desired.

A future direction for investigation suggests itself to be a study of the effects of temperature and pressure on the two constants, for interpolation and extrapolation of the equilibrium data of systems to various temperatures and pressures. Also, the equation, because of its simplicity, is anticipated to be particularly applicable to computer work.

ACKNOWLEDGMENT

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NOMENCLATURE

x: Mole fraction of component No. 1 in the liquid phase.
y: Mole fraction of component No. 1 in the vapor phase.
α: Relative volatility, as defined by equation [2].
γ: Raoult Law activity coefficient, as defined by equation [2*a*].
A, B: Empirical constants.

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THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XXX. THE HYDROGEN ENGINE AND DETONATION OF THE END GAS BY THE IGNITING EFFECT OF CARBON NUCLEI FORMED BY PYROLYSIS OF LUBRICATING OIL VAPOR[1]

By R. O. King[2] and S. V. Hayes[3]

ABSTRACT

Experiments with a C.F.R. spark ignition engine were carried out at compression ratios of 13 : 1 and lower. It was found that ignition and detonation of the mixture ahead of the flame front was due to its impregnation with finely divided carbon produced by the pyrolysis of the vapor of lubricating oil. The carbon accumulated on surfaces until in part dispersed into the hydrogen–air mixture by the entering turbulence. The carbon in the aerosol thus formed ignited at the relatively high temperature and pressure attained by the end gas in the conditions of the experiments. The onset of the consequent detonation and its severity at a particular engine speed was found to be dependent upon the factors of compression ratio, mixture strength, the initial compression temperature and that of the jacket coolant, the nature of the lubricating oil, and the rate at which it passed the piston into the combustion chamber or was supplied as an additive. Thus in the final experiment for which prevaporized cetane was used as an additive the shock of the accompanying detonation pressure waves was so great that the cylinder broke loose from the crank case because of the failure of the retaining casting.

INTRODUCTION

It was shown by experiments with hydrogen as the fuel for a C.F.R. Otto cycle engine (Part XXVII (1)), that preignition did not occur at a compression ratio of 10 : 1 when the exhaust valve was sodium-cooled and the spark plug was a cool running type. These experiments were carried out at engine speeds ranging from 900 to 1800 r.p.m. The jacket coolant was maintained at 100°F. and the air supply at 65°F. Mixtures ranging from 70% weak to 60% rich were used without the occurrence of detonation.

When the compression ratio was raised to 12 : 1, the top piston ring overlapped the three spark plug holes in the cylinder wall and lubricating oil passed into the combustion chamber at the positions of the holes at a rate greater than normal, as shown by the accumulation of soot on adjacent surfaces of the piston crown. Slight preignition then occurred infrequently when the engine was operated at 1800 r.p.m., although the jacket coolant had been reduced to 65° F. as a precautionary measure. When lower speeds at 1500 and 1200 r.p.m. were used, the frequency of preignition increased and backfiring as well as what appeared to be detonation occurred occasionally as mixture strength was increased to the correct value. These effects were avoided by allowing the engine to run for a few minutes on a weak

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[3]*Scientific Officer, Defence Research Board.*

mixture before using a correct or rich mixture in order to burn off excess carbon.

The experiments of this Part were carried out for the purpose of determining the operating conditions responsible for the occurrence of preignition and for detonation of the end gas by the igniting effect of carbon nuclei arising from pyrolysis of the vapor of lubricating oil passing the piston or supplied as an additive.

EXPERIMENTAL ARRANGEMENTS

The experiments were carried out with the C.F.R.-F4 engine that had been used for those described in Part XXVII (1). The exhaust valve was sodium-cooled. The cast iron piston was fitted with four pressure rings and one oil scraper ring. Ignition was by a cool variety of spark plug in the standard position but spark was not required after the exhaust valve had attained the requisite temperature. The temperature of the oil in the crank case was maintained at 140° F. The methods of regulating engine and mixture temperature and of metering rates of supply of air and hydrogen were as used for the experiments described in Part XXVII. Engine speed was maintained at 1200 r.p.m. except for the experiments described in Section IV. Mixtures are described as per cent weak or rich according to the percentage by which the hydrogen to air volume ratio is less or more than that required for a chemically correct mixture.

Oils Used as Lubricants or as Additives

Oils described as P.30 and P.10 were from a paraffin base crude and were graded by the supplier as S.A.E. 30 and S.A.E. 10 respectively. They were free of oxidation inhibitors or detergents. A synthetic oil, L.B. 300 X, is described as S.300. Cetane, $C_{16}H_{34}$, as obtained from the Eastman Kodak Co., was used as an additive only.

The terms "compression ratio" and "mixture strength" are abbreviated in subsequent text, as convenient, to C.R. and M.S. respectively, and compression ratios are stated as single numbers.

I. PRELIMINARY EXPERIMENTS

Compression ratios of 13.0 and 12.3 were used. Lubricating oil therefore passed the piston at a greater than normal rate at the positions of the three spark plug holes in the cylinder wall as was shown by the experiments of Part XXVII. Oils S.300 and P.10 were used when the C.R. was 13.0 and the jacket coolant maintained at 55° F. Oil S.300 only was used when the C.R. was 12.3 and the jacket coolant was raised to a temperature of 140° F.

Experimental Results, C.R. 13.0

Jacket Coolant 55° F., Mixture Supplied at 70° F., Speed 1200 r.p.m.

The experiment was started with a mixture 20% weak and the engine operated for 15 min. with spark timing adjusted to the optimum value. M.S. was then gradually increased and spark timing always adjusted to the

corresponding optimum until the engine continued to run without spark ignition. The crank case was always cleared of used oil and washed before it was filled to the standard level with a different variety. It appeared however that considerable "blow by" occurred at compression ratios used for the experiments. Thus after an oil had been used for 15 hr. running time it was found to have become blackened, presumably by impregnation with the carbon that had been formed in the combustion chamber and not retained in the standard oil filter of the engine; as a matter of some interest an experiment was carried out with oil S.300 that had been used for the running time mentioned. Experimental results are tabulated below.

TABLE I

Oil in crank case	M.S. required for detonation
S.300 fresh	Correct
S.300 used for 15 hr.	4.5% weak
P.10 fresh	8.0% weak

The results indicate that the vapor of oil S.300 is more resistant to pyrolysis than that of the paraffin base oil P.10 and that resistance diminishes as the oil becomes impregnated with the finely divided carbon.

Experimental Results, C.R. 12.3

Jacket Coolant 140° F., Mixture Supply 60° F., Speed 1200 r.p.m.

The crank case was drained of used oil and washed before it was filled to the standard level with fresh oil, S.300. Vaporization of oil deposited on surfaces in the combustion chamber was promoted by raising the temperature of the jacket coolant to 140° F. The experiment was started, as before, with a mixture 20% weak, which after 15 min. running time, was gradually increased while spark timing was adjusted to corresponding optimum values. The engine continued to run without spark ignition when M.S. had been increased to the correct value. Four indicator diagrams were then taken by means of a Photocon capacitance type of pressure pickup, the associated amplifier, and a Dumont oscilloscope. The diagrams are reproduced as Fig. 1. They show that, although a spark was not used, detonation occurred whilst combustion pressure was rising. The initiation of combustion must therefore have been due to the attainment of an igniting temperature by the surface of maximum temperature. This was necessarily that of the exhaust valve because the spark plug was an exceptionally cool variety and the detonation must have occurred in the end gas. The timing of surface ignition could not be regulated in conditions of a fixed C.R. and engine speed and was therefore somewhat irregular. The diagrams show that detonation occurred before t.d.c. in the circumstances. The engine continued to run but with power output reduced by approximately 30%. However the shock of detonation pressure waves occurring before t.d.c. was so severe that the experiment was discontinued after indicator diagrams had been taken.

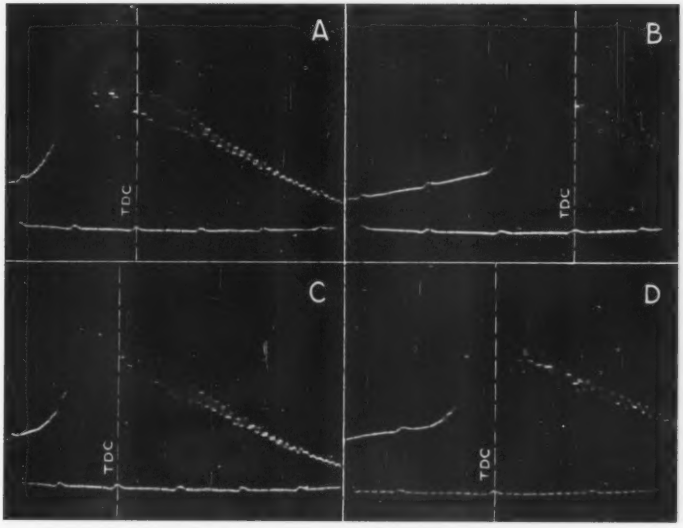

FIG. 1. Pressure–time diagrams, C.R. 12.3, 1200 r.p.m. Oil S.300 in crank case, jacket coolant 140° F., correct mixture supply at 60° F.

II. LUBRICATING OIL ADDED TO THE HYDROGEN–AIR MIXTURE AS A LIQUID

The experiments were carried out with a C.R. of 10.0 in order that the top piston ring should not lose its bearing on the cylinder wall at the spark plug holes. Lubricating oil from the crank case then passed the piston into the combustion chamber at the relatively low rate consequent on the cylinder and piston having been maintained in the conditions specified for the A.S.T.M.-C.F.R. method of knock rating.

Combustion of the vapor of oil added to the hydrogen–air mixture would be expected to yield an increase in power output. The rate of oil addition was therefore limited to 30 cc. per hr. This is equivalent to 1/70th of a drop of warm oil per cycle. A Bosch fuel injection system was tried but failed to operate until rate of oil supply was greater than 70 cc. per hr. It was then found that the Cox sampling device* could be adapted to deliver oil to the entering hydrogen–air mixture at suitable rates. This device is designed to take a sample of gas from any part of the engine cycle during a period of 1.0 millisecond. The direction of operation was reversed and lubricating oil injected into the cylinder during the induction stroke in order that it might be dispersed into the gaseous mixture by the random turbulence created at the inlet valve. It appeared however that the oil was deposited on the cylinder wall by the turbulence. Thus it was in the same state as that passing

**The device was supplied by Commercial Research Laboratory Inc., 20 Bartlett Avenue, Detroit 3, Michigan.*

into the combustion space from the crank case. Many experiments were carried out but results of special interest were not obtained.

The temperature of surfaces in the combustion chamber was then increased by raising that of the jacket coolant to 212° F. The rate of vaporization of oil deposits was thus increased and distribution of the vapor in the gaseous mixture was promoted by using a shrouded inlet valve to create a swirl in it. An experiment was carried out by the method described in Section I and when M.S. was increased to be 20% weak the engine ran without spark ignition but the timing of surface ignition as shown by the oscilloscope was extremely irregular. When nuclear ignition of the end gas occurred near t.d.c. the detonation shock wave was of great violence and the experiment ended when the Draper-Li pressure pickup, rated at 2000 lb. per sq. in., was crushed and the bronze bushing of the big end bearing was deformed.

III. THE DETONATION OF HYDROGEN–AIR MIXTURES BY CARBON NUCLEI DERIVED FROM LUBRICATING OIL AS SHOWN BY LIGHT INTENSITY DIAGRAMS

The light emitted by hydrogen burning in air is too low in intensity for photographic recording, irrespective of its concentration in the air. The light emitted by the burning of the vapor of lubricating oil in a homogeneous mixture with air is also too low in intensity for photographic recording when the concentration of air in the mixture is greater than required for complete combustion. The vapor of lubricating oil did not however form a homogeneous mixture with the gaseous mixture in the conditions of the experiments described in Section II and soot was deposited on surfaces in contact with flame even when the concentration of oxygen was in excess of that required for complete combustion. It was indicated by experiments described in Part XXVII (1) that the deposits built up as running continued until they were in part dispersed into the gaseous mixture by turbulence. Detonation would be caused by the soot becoming incandescent or pyrophoric at the temperature attained by the end gas, and light emission might be of sufficient intensity for photographic recording. Experiments carried out accordingly are described below.

Arrangements for Light Intensity Experiments

The viewing window, a short length of polished pyrex rod, occupied one of the spare holes in the cylinder wall. Light from the window was received by a photoelectric multiplier which provided a light intensity – time diagram on the screen of a dual-beam Dumont oscilloscope. The necessary spark ignition was by a cool plug in the standard position. The second spare hole was occupied by a "Sunbury" pressure pickup which provided a rate of pressure change – time diagram on the oscilloscope screen simultaneously with the light intensity – time diagram.

Conditions of Engine Operation

The hydrogen–air mixture was 55% weak. Engine speed was maintained at 900 r.p.m. by adjustment of load. The compression ratio was fixed at 10.0.

The temperature of the jacket was 212° F. and that of the mixture 70° F. A shrouded inlet valve was used to produce a swirl in the mixture. The crank case was cleared of used oil and then filled to the standard level with fresh S.300 oil. Oil P.30 as an additive was supplied by the Cox sampling device at the rate of 22.0 cc./hr.

Light Intensity and Rate of Pressure Change Diagrams

Photographs of diagrams which appeared simultaneously on the screen of the dual beam oscilloscope are reproduced as Fig. 2. The upper and lower horizontal traces on the diagrams are for part of the cycle in which there was no combustion. The lower trace is therefore for zero rate of pressure change

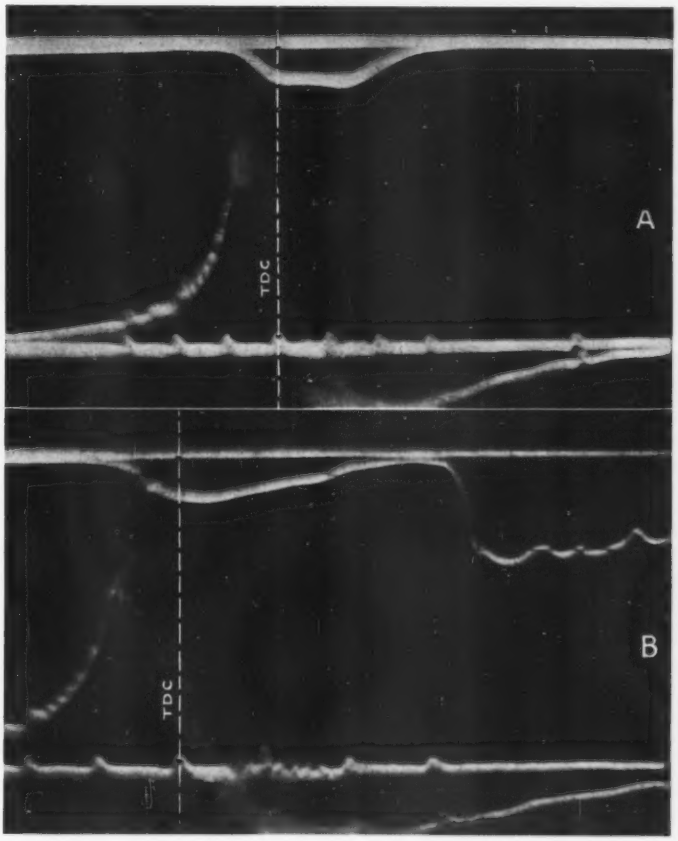

FIG. 2. Light intensity and rate of pressure change diagrams taken simultaneously C.R., 10.0. Oil S.300 in crank case, jacket coolant 212° F., speed 900 r.p.m., mixture 55% weak at 70° F.

A. No additive.
B. Oil P.30 added by Cox device at 22 cc./hr.

and the upper for zero light intensity. The light intensity trace extends down from the zero trace because a negative potential from the photoelectric multiplier was applied to the magnetizing coil of the related beam of the oscilloscope and the circuit to the multiplier completed through earth. The small "blips" on the lower trace are 10° of crank revolution apart and represent time intervals of 1.85 milliseconds at the engine speed 900 r.p.m., in respect of the upper as well as the lower horizontal trace. The blip at t.d.c. is marked by a broken vertical line. Combustion of the hydrogen is shown to be substantially complete at the time in degrees of crank revolution indicated by the intersection of the rate of pressure change trace with the horizontal trace for zero rate of pressure change. It is shown by both light intensity diagrams that the luminosity due to incandescent carbon particles appeared late in the combustion period and the rate of pressure change diagrams show that detonation then occurred.

Diagrams A.—These were taken before lubricating oil was supplied as an additive. The light intensity shown by the relevant diagram was then due to the incandescence of carbon particles that had been formed by pyrolysis of the vapor of oil S.300 that had passed the piston into the combustion chamber. The diagrams show luminosity beginning at 10° before t.d.c. with faint detonation pressure waves accompanying the igniting effect of the carbon particles. Combustion of the hydrogen was then well advanced and was substantially completed at approximately 5° after t.d.c. but luminosity due to the incandescence of free carbon continued until 15° after t.d.c. That is for 10° of crank revolution after combustion of the hydrogen had been completed.

Diagrams B.—These were taken while the paraffin base oil was supplied by the Cox sampling device as an additive, at the rate of 22 cc./hr. The diagrams show that luminosity appeared, as in the diagrams A, at approximately 10° before t.d.c. but the accompanying detonation pressure waves are more clearly defined. The pressure waves were not of sufficient energy to cause knock that was easily audible. Luminosity due to the incandescence of free carbon continued until it became zero at 45° after t.d.c., that is, for 40° of crank revolution after combustion of the hydrogen had been completed. Incandescence of free carbon then recurred with the emission of a relatively high level of light intensity which diminished slowly during the remaining time interval shown on the diagrams. The hydrogen–air mixture always contained some small proportion of oil vapor and the small pressure changes shown by the rate of pressure change diagrams before the occurrence of detonation and the later fuzziness of the diagrams are attributed to partial burning of the vapor.

The Recurrence of Luminosity

The finely divided carbon or soot formed by pyrolysis of the vapor of lubricating oil was of the nature of carbon black. It is known that the particle size in that material varies to an extent depending on the method of pyrolysis and the nature of the substance from which it was procured, and that the

freshly formed carbon possesses in a remarkable degree the power of absorbing gases. These characteristics may afford an explanation for the recurrence of luminosity during the expansion stroke of the engine, especially in view of the relatively large concentration of free oxygen then available because the hydrogen–air mixture supplied to the engine was 55% weak.

Oil S.300 passed the piston at the minimum practicable rate and it may be assumed that the carbon produced by pyrolysis was composed of extremely fine particles. Light was emitted for 15° of the expansion stroke only as shown by diagrams A and as there was no recurrence of luminosity it appears that all of the carbon was consumed by the oxygen then available.

The carbon produced by pyrolysis of hydrocarbons is known to contain both fine and coarse particles, thus when oil P.30 was used as an additive the burning of the fine particles and those produced by pyrolysis of oil S.300 passing the piston would account for the emission of light during 25° of the expansion stroke as shown by diagrams B. The subsequent occurrence of luminosity with a relatively high light intensity may be attributed to the burning of the coarser particles initiated by the adsorbed oxygen and sustained by the available free oxygen. The rate at which oil was vaporized was far from constant, when it was supplied as a liquid additive, and in some cases light emission was continuous although of variable intensity during the part of the expansion stroke shown on the diagrams.

IV. THE PREVAPORIZATION OF ADDITIVES AND EXPERIMENTS WITH CETANE

Experiments described in preceding sections demonstrated that the finely divided carbon responsible for detonation in the end gas was provided by the pyrolysis of the *vapor* of the lubricating oil. Vaporization involves a time factor, as represented by engine speed; thus whatever the rate at which oil passes the piston into the combustion chamber the proportion vaporized prior to spark ignition, at a particular speed, is not increased to a significant extent except by raising the temperature of surfaces to which the oil adheres as a liquid and thus inviting the occurrence of preignition due to the temperature attained by the exhaust valve. Thus it appeared that oil or cetane when used as an additive should be vaporized immediately prior to admission through the inlet valve, if results of an enhanced significance were to be obtained. A method of vaporization was therefore devised and used for experiments described in this Section.

The Methods of Vaporizing and Metering Small Rates of Supply of Liquid Additives

The vaporizing device and its arrangement for the discharge of vapor into the well of the inlet valve are shown by Fig. 3. The device comprises three concentric tubes. The outer one is of mild steel with an inside diameter of 0.30 in., and a perforation is provided in the blank lower end through which vapor of the additive is discharged. Within the outer tube is a concentric thin-walled steel tube having an outside diameter of 0.25 in. The annulus

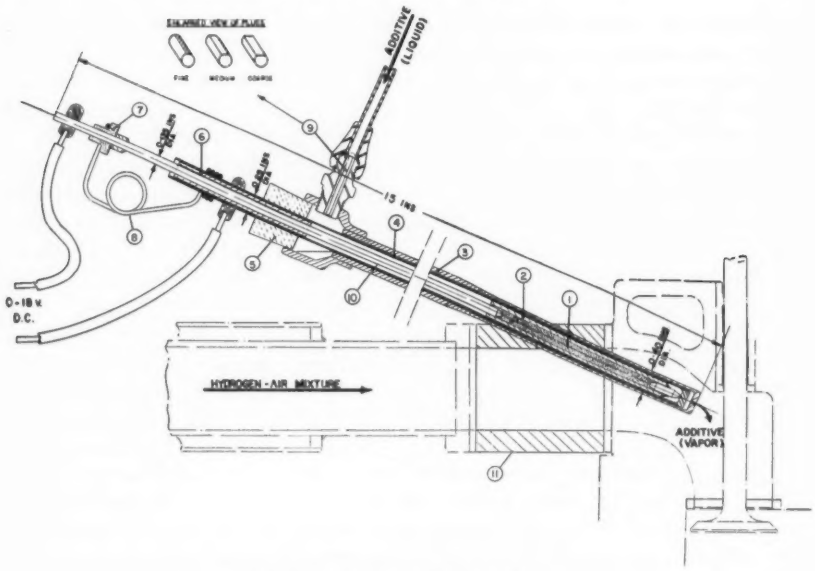

FIG. 3. Vaporizer for liquid additives.

1. Graphite powder
2. Silica tube
3. Outer steel tube
4. Inner steel tube
5. Vapor seal
6. Glass tube
7. Insulator
8. Spring
9. Flow restrictor
10. Steel electrode

formed by the two tubes is then 0.025 in. wide. The additive is supplied to the upper end of the annulus and is vaporized as it flows to the lower end by an electric heater enclosed in an inner concentric tube of silica. Powdered graphite is used as the resistor of the heater. The graphite forms part of an electric circuit completed in the device by a steel rod 0.125 in. in diameter projecting from the upper end and extending through the inner steel tube to make contact with the graphite. The rod is insulated by a length of glass tube from the inner steel tube. This tube connects with the lower end of the graphite resistor to complete the electrical circuit within the tube. The rate of heat supplied by the resistor is regulated by adjustment of the current supplied by a storage battery. The resistance of the graphite heater was 3.0 ohms, and 3.0 amp. were required to vaporize S.300 oil supplied at a rate of 30 cc./hr. If as much as 60% of the heat developed in the heater was radiated from the outer surface of the vaporizing device it would, if all absorbed by a correct hydrogen–air mixture supplied to the engine running at 900 r.p.m., raise its temperature by 2.5° F. only.

The device for the supply of additive to the vaporizing device at measured rates is shown by the diagram of Fig. 4. The rate of supply is controlled by adjustment of the air pressure in the receiver and further by the resistance plugs shown on Fig. 3. The rate is measured by timing the rate of fall of the

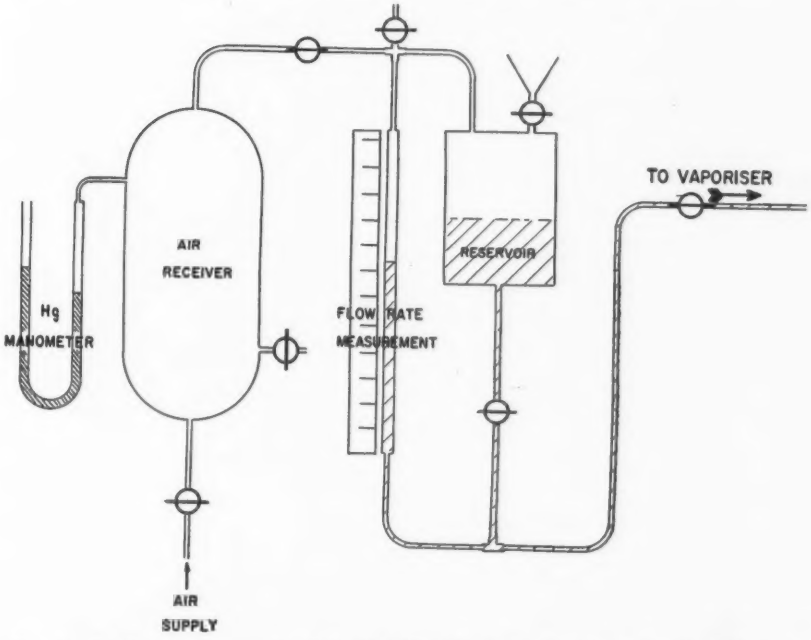

FIG. 4. Device for the supply of liquid additives to the vaporizer at measured rates.

additive in a graduated glass tube having an inside diameter at 4.0 mm. It was possible to measure accurately rates of additive supply as low as 3.0 cc./hr., and complete vaporization of the additive was obtainable with rates of supply greater than were required for experiment. The heating current was always regulated to be little greater than required for complete vaporization of the additive. The device was found to be suitable for the vaporization of lubricating oils as well as for additives with a unique boiling point. The results obtained when cetane was used are presently described. Those obtained when lubricating oils were prevaporized will be described in a subsequent paper.

Conditions Used for Experiments with Prevaporized Additives

Preliminary experiments with cetane demonstrated that detonation shock became extremely severe as mixture strength approached the correct value, and in consequence charge density was reduced by throttling to 64% of normal. Otherwise the conditions of experiment were as follows: compression ratio 10.0, engine speed 900 r.p.m., mixture temperature 110° F., and jacket coolant 212° F. Spark ignition, when used, was by a cool plug. Cetane was supplied to the vaporizer at the rate of 30 cc./hr. A Photocon pressure pickup with associated electronic equipment was used to obtain pressure–time diagrams.

Experimental Results with Cetane as an Additive

The engine was warmed up by running with spark ignition for 15 min. on a mixture 50% weak, with oil S.300 in the crank case. M.S. was then gradually increased and spark timing always adjusted to corresponding optimum values. A considerable degree of detonation was observed when M.S. had been increased to be 15% weak. Pressure–time diagrams were then taken at two-minute intervals for a period of eight minutes, and have been reproduced as Fig. 5 with t.d.c., marked by a vertical broken line. They show

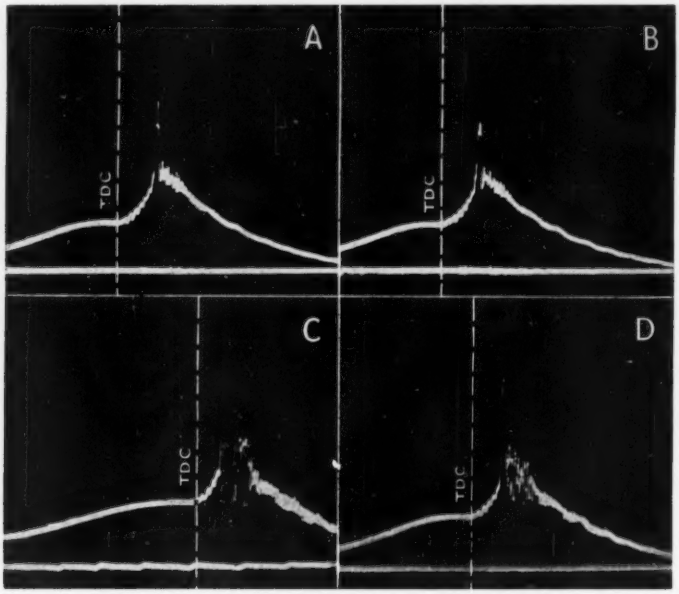

FIG. 5. Pressure-time diagrams taken at 2-min. intervals until spark ignition was replaced by surface ignition. C.R. 10, speed 900 r.p.m., jacket coolant 212° F., mixture 110° F. and 15% weak.

little variation in the time of occurrence of detonation, which always occurred after t.d.c., but show that the volume of end gas in which the effect occurred tended to increase. There was a corresponding increase in the amplitude of the gas vibrations which follow detonation pressure waves, and the engine continued to run when the spark was switched off.

Cetane was then supplied to the vaporizer at the rate of 30 cc./hr., and the four pressure–time diagrams reproduced as Fig. 6 were taken at half-minute intervals. They show that nuclear ignition accompanied by detonation pressure waves continued to occur in the end gas, and as combustion was not initiated by a spark it must have been initiated on the attainment of the requisite temperature by the exhaust valve, which provided the surface of maximum temperature in the combustion chamber. Thus the diagrams show that ignition timing was much less regular than when combustion was initiated by a spark, as would be expected.

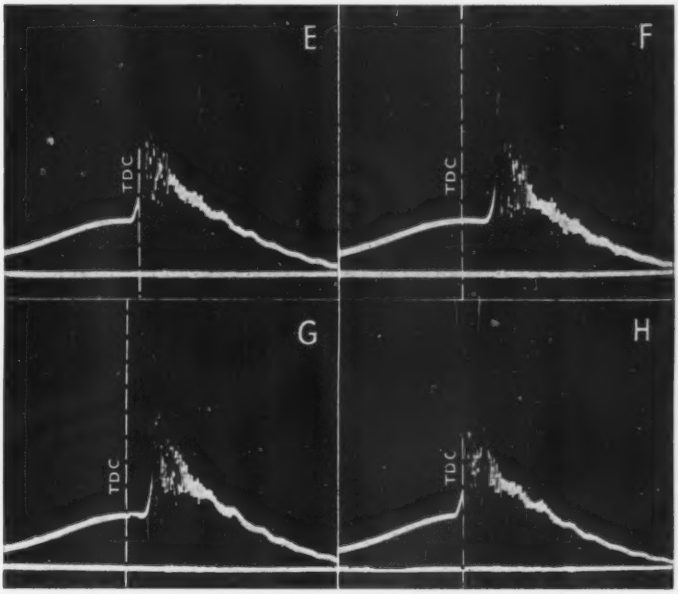

FIG. 6. Running continued with surface ignition and with addition of 30 cc./hr. of cetane prevaporized. Pressure–time diagrams taken at ½ min. intervals until cylinder broke loose from crank case.

It is shown by the last diagram taken that nuclear ignition accompanied by detonation pressure waves of large amplitude had occurred at t.d.c. The engine was unable to tolerate the consequent shock and the cylinder broke loose from the crank case because of the fracture of the retaining casting.

CONCLUSION

Experiments described in Part V (2) and Part XXVII (1) demonstrated that if an experiment were started with a clean combustion chamber, detonation did not occur until a deposit of soot arising from pyrolysis of lubricating oil vapor had built up on surfaces to such an extent that it was in part carried into the hydrogen–air mixture by turbulence. The consequent detonation occurred irregularly and a residue of soot always remained on surfaces in the combustion chamber.

It was concluded that detonation would not be dependent on a build-up of surface deposits of soot if the hydrogen–air mixture entering the cylinder carried the vapor of oil. The vaporizer described in Section IV *ante* was designed accordingly. Cetane, a standard fuel oil for the Diesel engine, was selected for experiments because of its unique boiling point, 549° F. The vapor was mixed with the hydrogen–air mixture by being ejected into the well of the inlet valve but it appeared that it formed a fog in the relatively cool gaseous mixture and that some might condense on surfaces before being dissipated by the heat of compression. The temperatures of surfaces were

therefore raised by maintaining the jacket coolant at 212° F. and the hydrogen–air mixture supply was maintained at 110° F. The mixture was 15% weak, engine speed 1200 r.p.m. Spark ignition was necessary and timing was adjusted to the optimum value, 3° in advance of t.d.c.

It is shown by the diagrams of Fig. 5 that combustion pressure rise began at t.d.c. approximately, and continued in the normal manner for about 5° of crank revolution. Detonation accompanied with large scale pressure waves then occurred in the end gas. The diagrams show that normal combustion and the subsequent detonation occurred with a high degree of regularity. They show also the small scale pressure waves known to follow spark ignition.

When the vapor of cetane was added to the mixture, running continued with spark ignition switched off. Thus it appeared that the temperature attained by the exhaust valve sufficed for the ignition. It is shown by the diagrams of Fig. 6 that combustion then proceeded in the normal manner for a brief and variable time interval before the occurrence of detonation in a corresponding volume of end gas. Thus it is shown by diagram E that detonation had occurred at t.d.c. in nearly the whole of the mixture, by diagrams F and G that detonation occurred after an appreciable interval of normal combustion, at from 5° to 10° after t.d.c., by diagram H, that detonation occurred again at t.d.c. in substantially the whole mixture. The diagrams of Fig. 6 were taken during a running period of two minutes. Thus combustion occurred 900 times while the hydrogen–air contained the vapor of cetane in the extremely small concentration provided by the supply of the liquid to the vaporizer at the rate of 30 cc./hr., i.e., 0.0011 cc. per cycle. The diagrams show that detonation may have occurred at t.d.c. in half of the combustion periods. It is not surprising therefore that the cylinder broke loose from the crank case after two minutes of running. The damage to the engine would have been regretted had it not provided a striking illustration of nuclear ignition of the end gas and its consequent detonation.

ACKNOWLEDGMENTS

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THE WASHING OF WAX FILTER CAKES[1]

By R. M. Butler and J. L. Tiedje

ABSTRACT

The problem of completely separating a finely divided solid from a slurry is frequently encountered in industrial processes. In the petroleum industry the problem occurs in solvent dewaxing and deoiling. Washed rotary filters, either singly or in combination, are normally used for such separations.

The total solvent requirements for a specified degree of oil removal depends on the filter arrangement and method of solvent application. On any individual filter, solvent may be applied in various proportions as dilution and wash. When more than one filter is used, the filters may be arranged either in series or parallel.

With a series arrangement fresh solvent may be supplied to each filter or a countercurrent system may be used with fresh solvent applied only to the final filter.

A number of these possible arrangements have been compared in the paper from the point of view of total solvent requirements. In the comparison of these, an equation has been developed for the degree of deoiling obtained during the washing of filter cakes. Experimental work is described which supports the theories discussed in the paper.

INTRODUCTION

When a solution of wax and oil in a solvent such as methyl *n*-propyl ketone (5) is cooled sufficiently, a solid wax phase crystallizes leaving the oil and some of the wax dissolved. Solvent dewaxing and wax recrystallization are operations of this type. The wax is normally separated from the mother liquor by means of rotary vacuum filters. Unfortunately, it is found that the filter cakes contain large quantities of liquid. Liquid to solids ratios in the range of 2 to 10 are common. In unwashed filters, this liquid is of the same composition as the filtrate and it follows that the solid wax will be contaminated with lower melting wax and oil when the solvent is removed by distillation.

In lubricating oil dewaxing, this has the disadvantage of reducing the yield of oil. In wax processing, dissolved wax and oil have an undesirable effect on the properties of the wax product (4). An analysis of the efficiency of various methods of washing the oil from the wax forms the subject of this paper. The methods are compared on the basis of solvent requirements for a given degree of deoiling.

Although the work is primarily concerned with the deoiling of wax cakes, it is probable that most of the equations can be applied to other processes involving filtration.

SINGLE FILTER

An obvious way to reduce the quantity of oil remaining in a wax cake is to increase the dilution of the slurry. This has the effect of reducing the concentration of oil in the liquid remaining in the pores of the filter cake and as a result reducing the quantity of oil remaining as an impurity.

[1]*Manuscript received September 21, 1956.*
Contribution from the Research Department, Imperial Oil Limited, Sarnia, Ontario.

The degree of deoiling which can be obtained from use of extra solvent dilution in the feed to a simple single filter may be calculated as follows:

For a given operation let
W be the volume of dry solid,
K the total volume of solvent used,
O the volume of oil in the feed,
O_P the volume of oil in the product,
and αW the volume of solvent in the final filter cake.

The liquid remaining in the cake must be of the same composition as the filtrate, i.e.,

$$O_P/\alpha W = O/K$$

or

[1] $$O_P/O = \alpha W/K\ .$$

This equation relates the degree of deoiling to the quantity of ketone and the cake dryness and enables the quantity of ketone to be calculated for any particular degree of deoiling.

A SERIES OF SIMPLE FILTERS WITH FRESH SOLVENT DILUTION BEFORE EACH FILTER

The solvent requirement may be decreased if a series of filters is employed with fresh solvent dilution being added to the wax stream before each filter. Such an arrangement is shown in Fig. 1.

If the quantities of wax, oil, and ketone leaving the nth filter are W, O_n, and αW respectively, then, from previous section, it follows that:

$$\frac{O_1}{O} = \frac{\alpha W}{K_1}\ ; \qquad \frac{O_2}{O_1} = \frac{\alpha W}{K_2+\alpha W}\ \frac{O_P}{O_{n-1}} = \frac{\alpha W}{K_n+\alpha W}\ .$$

Hence:

$$\frac{O_P}{O} = \frac{(\alpha W)^n}{K_1(K_2+\alpha W)\ \ldots\ (K_n+\alpha W)}\ .$$

It may be shown that for a given total quantity of ketone, K, the oil content of the product is a minimum when:

$$K_1 = K_2+\alpha W = \ \ldots\ = K_n+\alpha W.$$

For this optimum case

[2] $$\frac{O_P}{O} = \left(\frac{n\alpha W}{K+(n-1)\alpha W}\right)^n.$$

A COUNTERCURRENT CASCADE OF SIMPLE FILTERS

In the system described in the previous section, a series of filtrates of decreasing oil content is produced. A method of achieving a further reduction in solvent requirements is to employ filtrate from each stage as dilution for the preceding stage. When this is done, fresh solvent is only added to the final stage. A countercurrent cascade of this type is shown in Fig. 2.
The symbols used in this figure are the same as those in the previous sections.

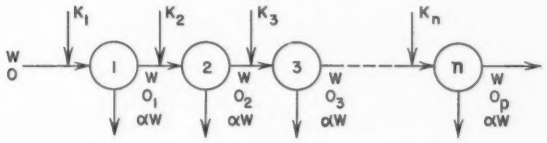


FIG. 1

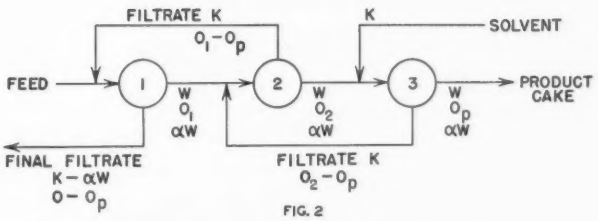


FIG. 2

FIG. 1. Simple filters—series parallel arrangement.
FIG. 2. Diagram of countercurrent cascade of simple filters.

The filtrate leaving any particular stage will be of the same composition as the liquid entrained in the cake. This is true for simple filtration; the more efficient conditions obtained in washed filters will be discussed later. It follows that:

$$\frac{O_1}{\alpha W} = \frac{O-O_P}{K-\alpha W}, \qquad O_1 = \left(\frac{O-O_P}{K-\alpha W}\right)\alpha W;$$

$$\frac{O_2}{\alpha W} = \frac{O_1-O_P}{K}, \qquad O_2 = (O_1-O_P)\frac{\alpha W}{K}$$

$$= \frac{(O-O_P)(\alpha W)^2}{K(K-\alpha W)} - \frac{O_P \alpha W}{K};$$

$$\frac{O_P}{\alpha W} = \frac{O_2-O_P}{K}, \qquad O_P = (O_2 - O_P)\frac{\alpha W}{K}$$

$$= \frac{(O-O_P)(\alpha W)^3}{K^2(K-\alpha W)} - O_P\left(\frac{\alpha W}{K}\right)^2 - O_P\frac{\alpha W}{K}.$$

Hence

$$O_P\left(1+\frac{\alpha W}{K}+\left(\frac{\alpha W}{K}\right)^2+\frac{(\alpha W)^3}{K^2(K-\alpha W)}\right) = \frac{O(\alpha W)^3}{K^2(K-\alpha W)}.$$

For n stages the result would have been:

$$O_P\left\{1+\frac{\alpha W}{K}+\left(\frac{\alpha W}{K}\right)^2 \cdots \left(\frac{\alpha W}{K}\right)^{n-1}+\frac{(\alpha W)^n}{K^{n-1}(K-\alpha W)}\right\} = \frac{O(\alpha W)^n}{K^{n-1}(K-\alpha W)}$$

or, summing the geometric series:

$$O_P\left\{\frac{1-(\alpha W/K)^n}{1-\alpha W/K}+\frac{(\alpha W/K)^n}{1-\alpha W/K}\right\} = \frac{O(\alpha W/K)^n}{1-\alpha W/K}$$

which reduces to:

[3] $$O_P/O = (\alpha W/K)^n.$$

A comparison of equation [3] with equation [2] shows that for a given degree of deoiling the solvent requirement for the series parallel filter arrangement is reduced by a factor slightly larger than $1/n$. The reason why the the factor is greater than $1/n$ is that in the countercurrent system the solvent used in each stage except the last already contains some oil and is thus slightly less effective than fresh solvent. However, a large saving is achieved by employing a countercurrent system.

Equation [3] has been plotted in Fig. 3. It may be seen that increasing

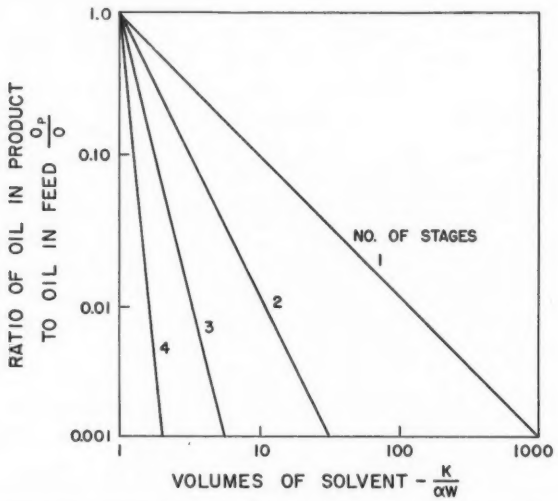


FIG. 3. Solvent requirements for deoiling in a countercurrent cascade of simple filters.

the number of stages in a countercurrent system greatly decreases the solvent requirement for a given degree of deoiling.

REMOVAL OF OIL BY DISPLACEMENT WASHING

A further economy can be made if some of the solvent is applied as wash after the cake has formed on the filter. The washing process is particularly effective since it is largely one of displacement rather than dilution. The wash liquid behaves like a piston pushing the cake liquid ahead of it. The picture is complicated by the fact that the liquid flows in laminar rather than plug flow. The effect which the laminar velocity distribution has upon a displacement washing process is considered below.

It is first assumed that washing takes place solely by the mechanical displacement of the fluid initially present and that the passages in the bed may be represented by uniform cylindrical capillaries. Since the flow of liquid in these capillaries will be streamline, the fluid velocity will vary parabolically across the diameter of the capillary and will be zero at the wall and a maxi-

mum in the center. The original filtrate, which happened to be at the axis of the capillary, will be displaced and move more rapidly than that which was near to the wall.

A typical capillary is shown at an intermediate stage of washing in Fig. 4. In this figure, L represents the thickness of the filter cake and R the radius of the capillary.

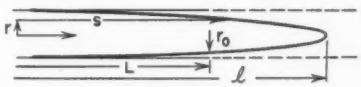


FIG. 4. Displacement of filtrate from capillary.

For mathematical convenience, it is assumed that the capillary extends indefinitely past L. This does not affect the result since it is only the removal of filtrate from the initial length L which appears in the final equation.

After a certain time during which the wash has travelled a distance l along the axis of the tube (l may be less or greater than L) the boundary between the wash and the original filtrate will be given by:

$$S = l\left(1-\frac{r^2}{R^2}\right)$$

where S, l, and r are as shown in Fig. 4.

The total volume of wash which has been introduced is:

$$V = \int_0^l \pi r^2 dS = \int_R^0 \frac{\pi r^2 l \cdot 2r dr}{R^2}$$

$$= \frac{\pi R^2 l}{2}.$$

Up to the stage where $l = L$, the liquid displaced from the capillary will be of the same composition as the original filtrate. After this point (breakthrough) the liquid leaving the capillary will be partly original filtrate and partly fresh wash.

Breakthrough occurs when a volume of wash equal to $\pi R^2 L/2$ has been introduced. This volume is exactly half of the original volume of filtrate retained in the cake.

If the cake initially contains O_A of oil and αW of cake liquids, then after a quantity of ketone K is applied as wash,

oil displaced $= O_A K/\alpha W$,

oil remaining $= O_A (1-K/\alpha W)$,

fraction of original oil remaining after washing $= (1-K/\alpha W)$.

This is true up to the breakthrough point when $K = \alpha W/2$ i.e., for the range $0 \leqslant K/\alpha W \leqslant \frac{1}{2}$. Up to this breakthrough point when half of the original filtrate has been displaced, the results of the washing process are identical with those predicted from the simple piston displacement theory.

After breakthrough the volume of displaced liquid is given by:

$$V_0 = \int_0^L \pi r^2 ds = \int_R^{r_0} \frac{-2\pi l r^3 dr}{R^2}$$

which reduces to:

$$V_0 = -\left|\frac{\pi r^4 l}{2R^2}\right|_R^{r_0}$$

$$= \frac{\pi R^2 l}{2} - \frac{\pi R^2 l}{2}\left(1-\frac{L}{l}\right)^2.$$

Volume of initial liquid remaining:

$$= \pi R^2 L - \frac{\pi R^2 l}{2} + \frac{\pi R^2 l}{2}\left(1-\frac{L}{l}\right)^2$$

$$= \pi R^2 L\left(\frac{L}{2l}\right).$$

Fraction of original filtrate remaining $= L/2l$.

But $\alpha W/K = 2L/l$.

Hence fraction of original oil remaining

[4] $$= O_P/O_A = \alpha W/4K.$$

In Fig. 5, the degree of deoiling obtained in washing a variety of wax filter cakes in the laboratory has been compared with the theoretical relation. The laboratory experiments agree with the theoretical curve up to the breakthrough point. It may also be seen that the experimental points diverge from the curve for piston displacement at the theoretical breakthrough point. For large quantities of wash, however, the degree of deoiling obtained experimentally is greater than the theoretical.

It is probable that the radial diffusion of oil into the wash stream in the core of the capillaries is the cause of this discrepancy. Thus, at the breakthrough point, the wash which leaves the center of the capillary will not still be pure solvent as was previously assumed but will contain oil which has diffused into the wash stream. This radial diffusion causes the washing to be more complete.

The mixing of liquids in streamline flow in capillaries has been considered both theoretically and experimentally by Taylor (3). If Taylor's equation [29] is converted to the symbols which are used in this paper, it becomes

[5] $$\frac{C}{C_0} = \frac{1}{2}+\frac{1}{2}\operatorname{erf}\left\{3.45\left[\left(\frac{\alpha W}{K}\right)^{\frac{1}{3}}\frac{x}{L}-\left(\frac{K}{\alpha W}\right)^{\frac{1}{3}}\right]\left(\frac{DT}{R^2}\right)^{\frac{1}{3}}\right\}$$

for $x/L < K/\alpha W$,

and

$$\frac{C}{C_0} = \frac{1}{2}-\frac{1}{2}\operatorname{erf}\left\{3.45\left[\left(\frac{\alpha W}{K}\right)^{\frac{1}{3}}\frac{x}{L}-\left(\frac{K}{\alpha W}\right)^{\frac{1}{3}}\right]\left(\frac{DT}{R^2}\right)^{\frac{1}{3}}\right\}$$

for $x/L > K/\alpha W$,

where $$\operatorname{erf} z = 2\pi^{-\frac{1}{2}}\int_0^z e^{-z^2} dz,$$

C_0 is the initial concentration of oil in the filtrate,

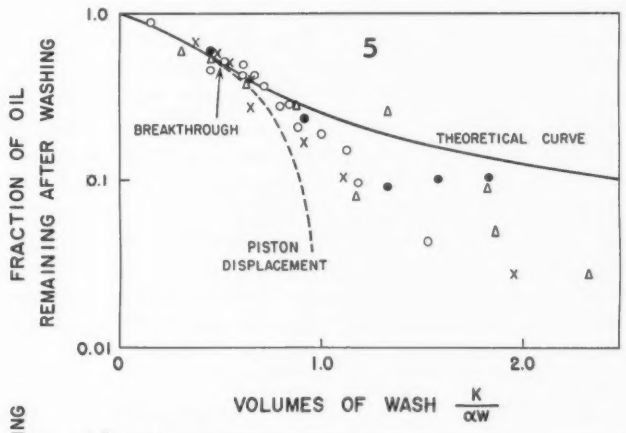
C is the average concentration of oil in the liquid across a section a distance x from the entrance to the capillary at a time when a quantity K of wash has been introduced,

D is the diffusion coefficient of oil in the liquid,

T is the time for αW of liquid to flow into the cake (a measure of the rate of washing).

Equation [5] only applies when $DT/R^2 \gg 0.1$.

For any particular quantity of wash (i.e., value of $K/\alpha W$) and wash rate (i.e., value of DT/R^2) the fraction of the original quantity of oil remaining may be determined from equation [5] and the following relation,



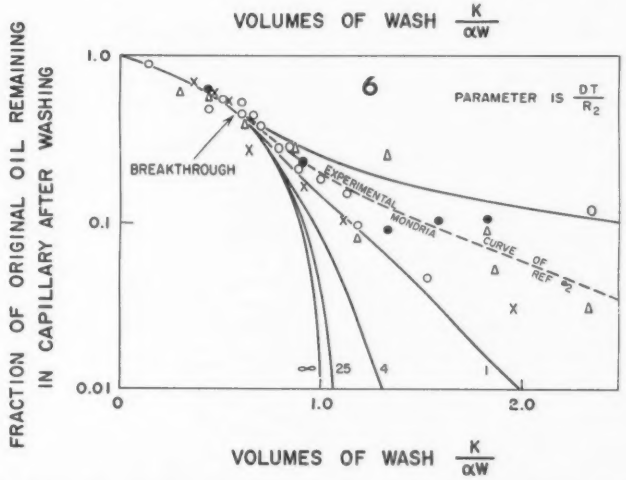


FIG. 5. Comparison of laboratory filter washing data with theoretical wash relation.
FIG. 6. Predicted effect of the diffusion parameter upon the degree of washing.

$$[6] \qquad \frac{O_P}{O_A} = \int_0^1 \frac{C}{C_0} d\left(\frac{x}{L}\right).$$

This integral has been solved graphically for a number of values of $K/\alpha W$ and DT/R^2 and the curves shown in Fig. 6 have been drawn from the results. Unfortunately, because of the limitation of the range for which equation [5] is applicable, it was not possible to draw curves for values of DT/R^2 less than unity. The curve for DT/R^2 equal to zero is, of course, the same as that derived previously.

It is interesting to note that for comparatively large quantities of wash, the theoretical oil content of the washed cake depends largely upon the parameter, DT/R^2. Of the quantities in this parameter, T is the one which can be most readily varied. This may be done by either varying the vacuum or the thickness of the cake. Work is now being carried out in these laboratories to check whether these large predicted variations in O_P/O_A can be obtained experimentally.

The results of the laboratory washing experiments have been plotted in Fig. 6 together with an experimental curve given by Mondria (2) for the washing of wax cakes with MEK – benzol mixtures. It may be seen that Mondria's curve and the experimental results are in agreement and that they correspond to a value of DT/R^2 of somewhat less than 1; DT/R^2 becomes equal to unity if D is of the order of 10^{-6} cm.^{2}/sec., T is 36 seconds, and R is 0.006 cm. Calculations of R from the rate at which wash liquid flows through the cake by means of the Kozeny equation (1) gave values of approximately one-tenth of this figure. A consideration of the mechanism of flow in actual filter cakes as compared to cylindrical capillaries offers an explanation for this difference. During the washing process, flow will not occur uniformly in all the pore space in the cake. Some cavities in the cake will be relatively stagnant and in order for the oil to be washed from these it must first diffuse into the stream of flowing fluid. This diffusion must occur over distances considerably greater than the average radius of the pores through which the wash is flowing. Fig. 7 shows how this can occur. Nevertheless the mecha-

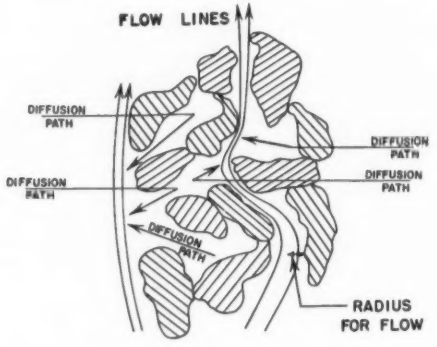


FIG. 7. Section through hypothetical filter cake.

nism is essentially one of diffusion into a moving stream similar to that described for the washing of cylindrical capillaries.

A SINGLE WASHED FILTER

In the previous sections, the quantity of solvent has been related to the degree of deoiling obtained during the filtration and washing processes. In this and subsequent sections, the two types of relations are combined to provide equations for various arrangements of washed filters. A single washed filter will be considered first.

In the last section it was shown that for laboratory filter leaf experiments the wash was more effective than would be predicted from the simple displacement equation [4]. However, when wash is applied to commercial rotary filters it is less effective than in the more carefully controlled laboratory experiments because of difficulties in obtaining uniform distribution. It is believed that the simple displacement equation is adequate for plant design purposes. This equation will be used in the following work.

Let W be the quantity of wax in the charge,
O the quantity of oil in the charge,
α_W the ratio of ketone to solid wax in the wet cake,
K_A the quantity of ketone used for dilution,
K_B the quantity of ketone used for wash,
K the total quantity of ketone used,
O_A the quantity of oil in the cake after filtration and before washing,
O_P the quantity of oil in the product.

Then,

[1] $$O_A = (\alpha_W W/K_A)\, O \text{ for filtration}$$

and

[4] $$O_P = (\alpha_W W/4K_B)\, O_A \text{ for washing.}$$

Hence,

[7] $$O_P/O = (\alpha_W W)^2/4K_A K_B \text{ for filtration plus washing.}$$

From Equation [7], it is apparent that for a given quantity of ketone the minimum value of O_P/O (i.e., maximum degree of deoiling) is obtained when:

$$K_A = K_B = K/2.$$

In this optimum case [7] becomes

[8] $$O_P/O = (\alpha_W W/K)^2$$

and it may be seen that the washed filter behaves as two simple stages.

Fig. 8 is a plot of Equation [7]. The fraction of the original oil remaining after washing is plotted on the logarithmic vertical axis and the number of volumes of wash $K_B/\alpha_W W$ on the horizontal axis. Curves have been drawn for various total quantities of solvent. It will be noted that the oil remaining in the cake is relatively high when no solvent is used as wash and that it

falls rapidly as an increasing fraction of the solvent is used for wash. An optimum is reached when half of the solvent is wash and half is dilution. From a practical point of view it is interesting to observe that the split between wash and dilution has little effect provided that the quantity of wash is between 40 and 60% of the total solvent.

In Fig. 9, the over-all oil ratios found in the same series of laboratory deoiling experiments described in Fig. 6 are plotted against the theoretical oil ratio calculated from Equation [7]. As would be expected, the theory tends to be conservative for high quantities of wash. Plant results are found to be closer to the theoretical line.

COUNTERCURRENT CASCADE OF WASHED FILTERS

In the previous section it was shown that the degree of deoiling obtained by a single washed filter without drying was given by:

$$[8] \qquad O_P/O = (\alpha_w W/K)^2$$

when half of the ketone was applied as wash and half as dilution. However, it was also shown that the split between wash and dilution had little effect if the quantity of wash was kept between 40% and 60% of the total.

A comparison of equations [6] and [2] shows that a washed filter with optimum wash dilution ratio behaves as two theoretical stages. It follows that a cascade of n washed stages will produce approximately the same separation as $2n$ simple stages. The degree of deoiling for such a cascade will be given by:

$$[9] \qquad O_P/O = (\alpha_w W/K)^{2n} \text{ for } n \text{ washed filters and no drying.}$$

This equation does not take into account the extra deoiling which will be obtained by the drying on top of the filters. An allowance may be made for this by multiplying the over-all oil ratio by α_D/α_w for each filter with the result

$$[10] \qquad O_P/O = (\alpha_w \alpha_D W^2/K^2)^n \text{ for } n \text{ washed filters with drying.}$$

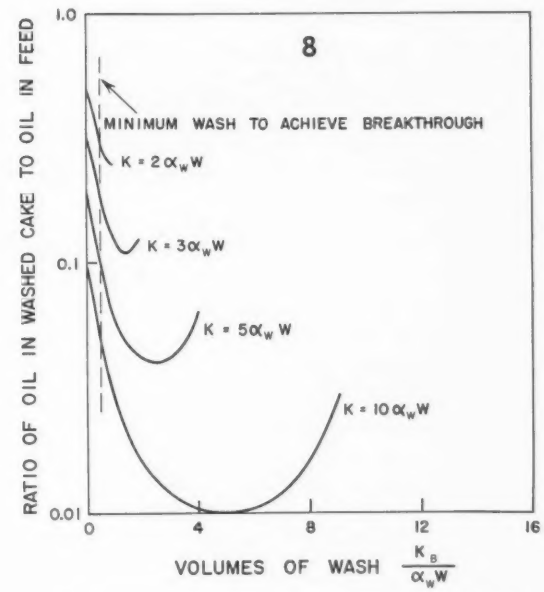
In this equation α_D is the value of α for the dried cake.

Equation [10] will not be quite exact because:

(*a*) It does not take into account the extra deoiling which will be produced by the ketone displaced during the drying operation when it is applied to the preceding filter in the cascade as wash and dilution.

(*b*) In some cases the deoiling obtained during drying may be greater than shown since the oil is concentrated towards the bottom of the filter cake during the washing operation.

Equation [10] is suitable, however, for estimating the quantity of ketone which will be required in practical cases.



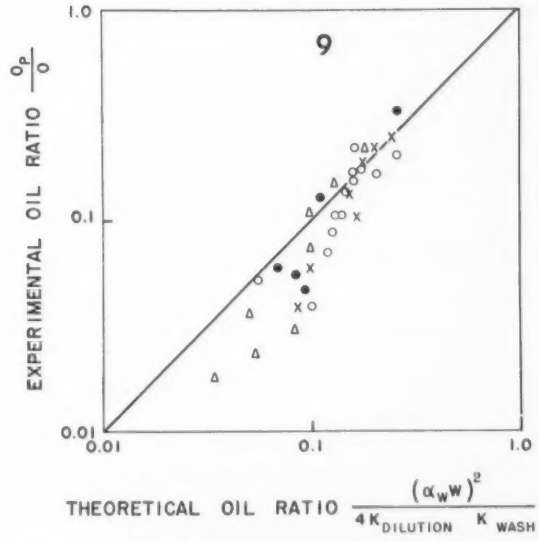


FIG. 8. The effect of varying the distribution of solvent between dilution and wash.
FIG. 9. Comparison of predicted oil ratios with those obtained in laboratory filter leaf experiments.

SERIES ARRANGEMENT OF WASHED FILTERS

The following equation may be developed for this arrangement:

$$[11] \qquad \frac{O_P}{O} = \left(\frac{n^2\alpha_D\alpha_w W^2}{[K+(n-1)\,\alpha_D W]^2}\right)^n.$$

This equation is for the optimum distribution of solvent, which occurs when the total quantity of solvent fed to each filter (i.e., the fresh solvent plus the solvent in the cake from the previous filter) is the same and is equally distributed between dilution and wash.

COMPARISON OF DIFFERENT FILTER ARRANGEMENTS

A specific numerical problem is considered in this section and the solvent requirements for different filter arrangements are compared in Table I.

The problem may be stated as follows:

It is required to estimate the over-all solvent to feed ratio for the deoiling of a certain slack wax given the following data:

oil content of slack	=	12.5%
dry wax yield	=	100%
oil content of product	=	0.3%
α_w	=	6.5
α_D	=	4.0

This is a fairly typical problem which might occur in the design of a wax processing plant.

The solution will be considered for the case of two countercurrent washed stages.

Solution: basis 1 lb. of slack*

O	= 0.125 lb.
W	= (1−0.125)×1.00 = 0.875 lb.
O_P	= (0.003/0.997)×0.875 = 0.00263 lb.
O_P/O	= 0.00263/0.124 = 0.021

For two countercurrent washed stages,

$$O_P/O = (\alpha_w\alpha_D\ W/K^2)^2$$

hence

$$K = 0.875\sqrt{6.5\times4.0}/0.021^{1/4} = 11.7.$$

Solutions of the problem for other numbers of filters and filter arrangements are compared in Table I.

The washing of filters decreases the solvent requirements markedly. Thus it may be seen that one washed filter is approximately equivalent to a series of three simple filters with fresh solvent dilution before each and is nearly equivalent to two simple filters in a countercurrent cascade. In practice washed filters are nearly always employed.

**In this problem, weight ratios are taken to be identical with the corresponding volume ratios. In most practical wax, oil, and ketone systems, the densities are nearly the same and this assumption is essentially true.*

TABLE I

SOLVENT TO FEED RATIO REQUIRED FOR A GIVEN DEGREE OF DEOILING

No. of stages	Simple filters		Washed filters	
	Series	Countercurrent	Series	Countercurrent
3	31.0	12.7	18.4	8.5
2	44.8	24.1	19.9	11.7
1	167	167	30.8	30.8

A countercurrent system is more efficient than a series arrangement. For two washed stages the countercurrent system only requires 59% of the solvent that is necessary for the series case.

TABLE OF SYMBOLS

C Average concentration of oil in liquid across a section of capillary.
C_0 Initial concentration of oil in liquid in capillary.
D Diffusion coefficient of oil in solution.
K Quantity of solvent.
K_A Quantity of solvent used as dilution.
K_B Quantity of solvent used as wash.
K_1, K_2, etc. Total solvent fed to first filter, second filter, etc.
L Length of capillary (thickness of bed).
O Quantity of oil in feed.
O_A Quantity of oil in cake after filtration and before washing.
O_P Quantity of oil in product.
O_1, O_2, etc. Quantity of oil in cake from first filter, second filter, etc.
R Radius of capillary.
T Time required for αw of wash to flow into cake.
W Quantity of dry wax.
l Maximum distance wash has travelled along capillary.
n Number of stages in filter arrangement.
r Distance from center of capillary.
s Distance fresh wash has travelled along the capillary—a function of r.
x Distance along capillary.
z Arbitrary variable.
α Ratio of solvent to solids in cake.
α_w Value of α for wet cake.
α_D Value of α for dried cake.

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VAPOR-LIQUID EQUILIBRIUM DATA FOR SYSTEMS METHANOL–TOLUENE AND *n*-PROPANOL–TOLUENE[1]

By Benjamin C.-Y. Lu

ABSTRACT

Vapor–liquid equilibrium data have been obtained on the systems methanol–toluene and *n*-propanol–toluene at atmospheric pressure in a Colburn still.

Azeotropes have been found at 0.875 mole fraction methanol and 0.620 mole fraction *n*-propanol in the systems methanol–toluene and *n*-propanol–toluene respectively.

Activity coefficients have been calculated. The thermodynamic consistency of the data has been checked by the Redlich-Kister relationship with an overall deviation of 6% in both cases.

INTRODUCTION

Vapor–liquid equilibrium data of alcohols and hydrocarbons are of particular interest in extractive and azeotropic distillation work. In the present investigation the vapor–liquid equilibrium relationships were determined for the binary systems methanol–toluene and *n*-propanol–toluene at atmospheric pressure.

Data on both systems have been reported only once previously (1, 3) and their accuracy is in doubt. Benedict *et al.* (1) employed the dynamic distillation method in the simplest manner to determine the vapor–liquid equilibrium data for the system methanol–toluene at atmospheric pressure. The composition of the distillate and the liquid in the still changes during such a distillation, and the samples represent the average values. In order to reduce this composition variation, Benedict *et al.* (1) employed a large quantity of liquid in the still in comparison to the quantity of the distillate. However, this modification may be offset considerably by the high relative volatility of methanol and toluene. Robinson and Gilliland (8) reviewed the experimental data obtained by this method and stated that in a few systems significant difference had been found in the composition between the vapor obtained in this manner and the true equilibrium.

Bonauguri *et al.* (3) employed an Othmer still (6) to determine the vapor–liquid equilibrium data for the system *n*-propanol–toluene at atmospheric pressure. The vapor–liquid equilibrium data reported are not complete. No liquid temperature was included.

Furthermore, there is appreciable discrepancy on the composition of the binary azeotrope between the data reported by Benedict *et al.* (1) and Bonauguri *et al.* (3) and the data compiled by Horsley (4). For the above reasons, it seems to be desirable to redetermine the vapor–liquid equilibrium data for the two systems.

[1]*Manuscript received September 26, 1956.*
Contribution from the Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario.

MATERIAL

The certified grade, sulphur-free toluene was supplied by the British Drug Houses and was purified by redistillation. The fraction used in this work had a refractive index n_D^{25} of 1.4940, which is comparable with the value of 1.49414 as reported in the literature (10).

The spectro grade methanol was supplied by the Fisher Scientific Company and was used without any further purification. The refractive index n_D^{25} was 1.3266, which is in agreement with the value reported in the literature (10).

The certified grade *n*-propanol was supplied by the Fisher Scientific Company and was purified by redistillation. The refractive index n_D^{25} of the fraction used was 1.3835, while the value reported in the literature is 1.38333 (10).

EXPERIMENTAL METHOD

The vapor–liquid equilibrium data were determined in a Colburn still (5). In order to obtain smooth operation, the unit was well insulated to minimize heat losses. The minimum time for a run was one hour. This was found to be sufficient to establish the equilibrium. Prior to the removal of the liquid and condensed vapor samples, a small amount of material was drained off through the sampling stopcocks and discarded. Compositions were determined by measuring the refractive indices at 25° C. (±0.1°) with a Spencer Abbe-type refractometer. The analyzed composition is accurate to within ±0.2 mole %.

RESULTS

Vapor–liquid equilibrium data have been obtained on methanol–toluene and *n*-propanol–toluene systems at atmospheric pressure. The activity coefficients of the liquid phase were calculated from the expression:

$$\gamma_i = y_i P / x_i P_i^0.$$

The vapor pressure data were taken from Stull's compilation (11). The experimental results and the calculated activity coefficients are tabulated in Tables I and II, and in graphical form as $x-y$ diagram in Figs. 1 and 2. The

TABLE I

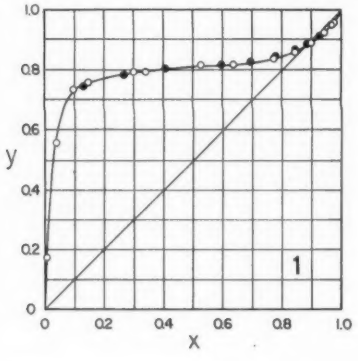
EXPERIMENTAL DATA: SYSTEM METHANOL–TOLUENE

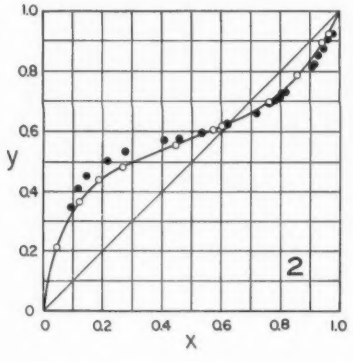
t° C.	x_1	y_1	γ_1	γ_2
103.6	0.006	0.172	7.31	1.02
84.4	0.037	0.557	7.45	1.06
71.5	0.097	0.736	5.84	1.04
68.9	0.147	0.758	4.35	1.09
66.4	0.299	0.794	2.47	1.24
65.7	0.340	0.795	2.25	1.35
64.9	0.525	0.813	1.53	1.75
64.5	0.637	0.818	1.30	2.25
63.8	0.771	0.837	1.13	3.30
63.7	0.842	0.859	1.06	4.19
63.6	0.899	0.887	1.03	5.28
63.7	0.943	0.922	1.02	6.42
64.0	0.966	0.949	1.01	6.91
64.2	0.914	0.958	1.00	7.31

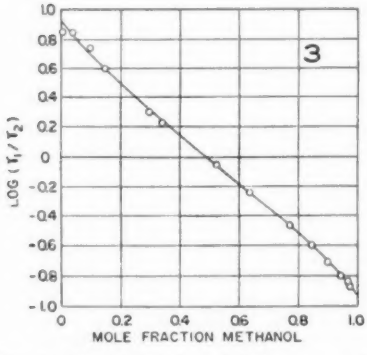
TABLE II

EXPERIMENTAL DATA: SYSTEM *n*-PROPANOL–TOLUENE

t° C.	x_1	y_1	γ_1	γ_2
104.1	0.046	0.211	3.59	1.00
98.4	0.121	0.366	2.95	1.03
96.3	0.188	0.440	2.50	1.05
94.2	0.268	0.482	2.09	1.15
93.4	0.444	0.556	1.50	1.33
92.8	0.571	0.603	1.29	1.58
92.6	0.600	0.617	1.28	1.65
92.9	0.762	0.699	1.12	2.15
93.5	0.804	0.728	1.08	2.31
93.9	0.858	0.786	1.07	2.48
95.5	0.940	0.897	1.05	2.66
95.8	0.961	0.921	1.04	3.13







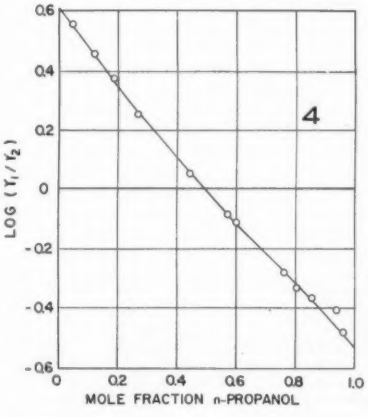


FIG. 1. Vapor–liquid equilibrium curve for methanol–toluene at atmospheric pressure.
○ Author
● Benedict *et al.* (1)

FIG. 2. Vapor–liquid equilibrium curve for *n*-propanol–toluene at atmospheric pressure.
○ Author
● Bonauguri *et al.* (3)

FIG. 3. Redlich-Kister test of thermodynamic consistency for methanol–toluene.

FIG. 4. Redlich-Kister test of thermodynamic consistency for *n*-propanol–toluene.

data reported by Benedict *et al.* (1) and Bonauguri *et al.* (3) are also included in the diagrams. Agreement is good between the data reported by Benedict *et al.* and the data obtained from the present studies for the system methanol–toluene over the entire range. The data of Bonauguri *et al.* (3) on the system *n*-propanol–toluene indicated a greater relative volatility of the more volatile component. This may be due to the refluxing of vapors in the Othmer still.

The binary azeotrope compositions have been determined as 0.875 mole fraction methanol at a temperature of 63.6° C. for the system methanol–toluene, and as 0.620 mole fraction *n*-propanol at a temperature of 92.6° C. for the system *n*-propanol–toluene. Comparison of these results with those of previous workers are shown in Tables III and IV.

TABLE III

METHANOL–TOLUENE BINARY AZEOTROPE AT ONE ATMOSPHERE

Composition, mole % methanol	B.p., ° C.	Ref.
86	63.8	(2,4)
89.6*	63.6*	(9)
88	63.6	(1)
87.5	63.6	Author

*Extrapolated value.

TABLE IV

n-PROPANOL–TOLUENE BINARY AZEOTROPE AT ONE ATMOSPHERE

Composition, mole % *n*-propanol	B.p., °C.	Ref.
54	92.6	(2,4)
62	—	(3)
61.5*	92.6*	(9)
62.0	92.6	Author

*Extrapolated value.

The thermodynamic consistency of the data has been checked by the method of Redlich and Kister (7). According to this method, with the assumptions that the vapor phase obeys the ideal gas laws and that the activity coefficients of the liquid phase are independent of temperature, the following equation may be employed.

$$\int_0^1 \log(\gamma_1/\gamma_2)\, dx_1 = 0$$

For each system, log γ_1/γ_2 is plotted against the mole fraction of component 1 in the liquid. These plots, as shown in Figs. 3 and 4, should give a curve crossing the log $\gamma_1/\gamma_2 = 0$ line, and cut off an equal area both above and below the line. Planimeter measurement indicated that the two areas agreed within 6% in both cases.

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NOMENCLATURE

P = total pressure, mm. of mercury,
P^0 = vapor pressure, mm. of mercury,
t = temperature, ° C.,
x = mole fraction in liquid phase,
y = mole fraction in vapor phase,
γ = liquid phase activity coefficient.

Subscripts

$_1$—refers to lower boiling component in the binary mixture, methanol in one case, *n*-propanol in the other.

$_2$—refers to higher boiling component in the binary mixture, toluene in both systems.

$_i$—refers to component 1 or 2.

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NOTES

PRESSURE TRANSDUCERS AS RECORDING MANOMETERS IN CHEMICAL KINETICS

By Paul A. Giguère and I. D. Liu

In studying the rate of gas-phase reactions by the static method, measurement of the pressure changes can be extremely tedious. Recording devices have been described which depend either on photographing the height of a mercury column (9) or on measuring the resistance of a wire stretched inside a mercurial manometer (8). Alternatively, balancing the mercury column by a rather elaborate servo-system has also been tried (5). None of these is suitable, however, when there is possibility of the mercury interfering with the reaction. In the absence of corrosive gases thin, flexible metal diaphragms or bellows may be used, coupled to some sort of electromechanical transducer based on variation of either resistance (3, 4), capacitance (6), or inductance (1, 2, 7).

Such instruments, known as pressure transducers, are now commercially available. We have used successfully some of the models manufactured by the Statham Laboratories* for an investigation of the thermal decomposition of hydrogen peroxide vapor. They contain an "unbonded wire" type of strain gauge and are available in a variety of pressure ranges from 2.5 mm. Hg up to several atmospheres. Their accuracy and linearity are within 1% of full scale and their resolution is better than 0.1%. They are usable at temperatures from −50° to 120° C.; over that range zero drift and sensitivity changes may be reduced to less than 1% by an optional compensation feature. The output (20 to 40 mv.) is sufficient to operate directly a recording potentiometer. Stainless steel or Monel construction is also available for use with mildly corrosive gases. Further protection was secured in our case by coating the inner surface of the transducer with a thin film of silicone vacuum oil.

Measurements of absolute pressures below about 100 mm. Hg require transducers of the differential type with the reference side evacuated. In that connection we have noticed that when the pressure on the reference side is reduced below about 1 mm. Hg the instruments give an erratic response presumably due to limiting heat convection from the fine strain-sensitive wires, which then act as a Pirani gauge. Operation *in vacuo* under the normal exciting voltage even resulted in burning of the wires in one instance. To overcome this difficulty a residual pressure of a couple of millimeters of mercury may be left on the static side or, more simply yet, the input voltage may be reduced to about 60% of its normal value, with corresponding reduction in the output. Care must be taken to prevent pressure overload beyond the maximum allowable (or the order of 100% of full scale).

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For work with extremely corrosive media we have combined a glass spoon gauge with a linear transducer capable of measuring small displacements and forces (± 0.03 mm. or ± 5 gm. full scale) in a direction perpendicular to the mounting base. To ensure absolute rigidity of the unit (Fig. 1) the transducer

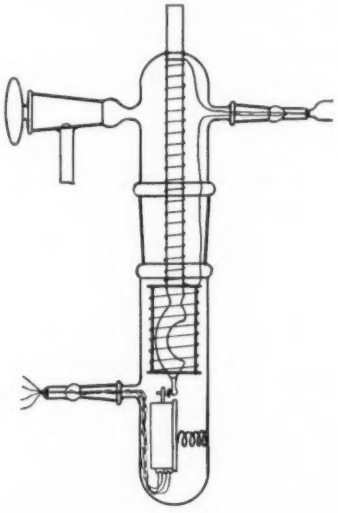

FIG. 1. Combination of glass spoon gauge with linear transducer for recording pressure changes in corrosive gases.

(Statham, Model G-7) was held against the walls of the glass tube (4 cm. diam.) by means of a coil spring, and the large ground-glass joint (45/50) was assembled with Apiezon W wax. The tiny flat-head screw traversing the linkage bar of the transducer could be brought in contact with the glass bead at the tip of the spoon gauge by means of a fine screwdriver inserted in the side tube. The latter also provided an outlet for the connecting wires. An adjustable stop (not shown) is advisable to minimize danger of breakage from accidental pressure surge in the reaction system. Because of the damping by the mechanical transducer this device is much less sensitive to vibrations than the glass spoon alone. The various models constructed had sensitivity of the order of 0.2 mv. per mm. Hg. The response was linear up to about 20 mm. Hg and the resolution was 0.1 mm. Hg over that range.

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